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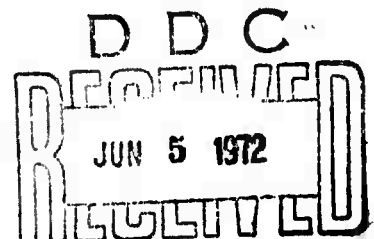
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Contacts Between Chalcogenide Glasses, Metals
and Semiconductors

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The Director,
Advanced Research Projects Agency,
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Contacts Between Chalcogenide Glasses, Metals
and Semiconductors

1. General Summary of Current Work

The two main purposes of the research here described are to elucidate the mechanism of threshold switching, and to explore systems with contact materials which can be electronically altered in situ. With this end in view, the experimental work performed during the last six months has concerned itself with the following problems:

- (a) the nature of the OFF-characteristic, with special reference to time-dependent conductances (current creep) and evidence for space charge polarization effects;
- (b) the analysis of switching delays, with and without overvoltage, in terms of thermal, nucleation and electronic models;
- (c) the characteristics of switching systems with crystalline semiconductor electrodes, with special reference to switching delay relationships and the possibility of third electrode control;
- (d) recovery after switching operation, and its relevance to the statistical aspects of threshold switching;
- (e) measurements of self-capacitance as a function of applied bias voltage; and
- (f) measurement of scaling relationships: switch parameters (be-

fore and after the first-ever switching event) as a function of film thickness.

2. Status Report

(items correspond to those listed above)

- (a) Recent pulse measurements have shown that the OFF characteristics of ovonic switches with nominally identical graphite electrodes do in fact display a small amount of rectification. Since two contacts are always involved, the observed asymmetry refers to the differences between the "reverse" characteristics of the two single contacts. The current differences for a given applied voltage amount from 0 to 50% in the two directions of current flow. When switching characteristics are displayed continuously under AC, these differences escape attention because the OFF-current is so small. Negative current creep is (typically by 10 to 20%) observed over periods 50 to 100 microseconds. This implies also differences of behavior, depending on whether switches are addressed by short pulses or prolonged voltage ramps. A short paper on this last matter has been prepared for publication and is reproduced at the end of this report (Appendix A).
- (b) A detailed scrutiny of the delay characteristics can lead to conclusions as to the nature of the switching process. The main point is the extraordinary constancy of the pre-switching current (for $V \approx V_{TH}$) during the switching delay. The matter is discussed in a short paper by Lee and Henisch (Appendix B).
- (c) Measurements have been performed on chalcogenide glass films, deposited on crystalline Ge surfaces and tested with graphite or

tungsten point contacts. Before any special role can be ascribed to the Ge-glass interface, it is necessary to clarify what the characteristics of the Ge-glass combination would be without such a role. This is done in a note by Vendura and Henisch (Appendix C). [This is a substantially revised and amplified version of Appendix B as featured in the Semi-Annual Technical Report of December 1, 1971.] The principal conclusion is that the Ge-glass interface behaves quite differently from the graphite-glass and W-glass interfaces. This has a bearing on the routine assumption that contact effects "do not matter" in threshold switching. The effect of carrier injection into the Ge by means of third electrodes has also been explored. Current and voltage gain can be observed in this way but, as far as could be ascertained, all of it is accounted for by the transistor-like nature of the Ge electrode assembly itself. There is no reason to believe that the glass film plays any special role in this. [This case should be clearly distinguished from that discussed by R. F. Shaw and co-workers, Appl. Phys. Lett. 20, 241 (1972), which deals with hot carrier injection.]

- (d) Matters relating to the recovery of threshold switches after cessation of an ON-state are also covered by Appendix D below.
- (e) Measurements of self-capacitance at a frequency of between 1 and 10 MHz have yielded a slight increase towards the threshold voltage, at any rate for the switches available for test. The negative capacitance behavior originally reported by Walsh, Vogel and Evans was not observed on these units. [The suggestion has been made that some switches show it and others not, depending on small differences of structure which are not yet understood.]

- (f) An extensive series of measurements on scaling relationships has been undertaken. The major difficulty and danger showed itself at an early stage: a wide distribution of results even for a given thickness. Entirely misleading conclusions can be drawn from measurements which are not performed on a proper statistical basis. On the other hand, and in view of the wide distributions observed, such statistical measurements would be very time-consuming. The matter remains under consideration.

3. Note on Personnel

In addition to the Principal Investigator, Dr. S. H. Lee (Research Associate), Mr. D. Burgess (Graduate Assistant) and Mr. R. W. Pryor (Graduate Assistant) have been employed on the contract, with Mr. G. J. Vendura, Jr. (Graduate Assistant) also involved, but not paid by contract funds.

Pre-threshold Conductance and Polarization Effects in
Amorphous Semiconductor Switches

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ABSTRACT

It is shown that the conductance and threshold parameters of threshold switches depend on the manner in which switching systems are addressed. Slow voltage ramps lead to internal polarization; fast square pulses do not. The polarization processes influence all switching operations performed sequentially; their room-temperature relaxation time is of the order of several milliseconds. The observations are interpreted on the basis of a space charge model involving injected carriers, subsequently trapped.

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1. Introduction

An understanding of the pre-threshold conduction mechanism is of obvious importance for our interpretation of threshold switching itself⁽¹⁻³⁾.

Two important issues arise:

- (a) Different switching mechanisms imply different scaling relationships, i. e. different variations of threshold voltage, threshold current and pre-threshold characteristics with the thickness of the amorphous film. It was found, however, that scaling relationships, far from being uniquely determined, depend on the procedure employed in measuring the electrical parameters. In particular, the pre-threshold conductance depends on the immediate electrical history of the system and thus on the "mode of address," as will be shown below.
- (b) In the belief that contact effects are unimportant, measured conductances have often been interpreted^(4, 5) in terms of bulk conductivities, e. g. in accordance with expressions of the form

$$\sigma = \sigma_0 \exp \left[-\frac{\Delta E}{kT} + \frac{F}{F_0} \right]$$

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where ΔE is a thermal activation energy, F is the local field and F_0 a field constant. Since the local field within the amorphous layer is not independently known, such an expression can be tested only by reference to the average applied field, and this involves the assumption of field uniformity. In turn, this assumes that space charge effects are totally absent, with all the corresponding dangers of circular argumentation.

"Mode-of-address" effects call for clarification in both contexts. Measurements were carried out on encapsulated threshold switches of $\text{Te}_{40}\text{As}_{35}\text{Ge}_7\text{Si}_{18}$, deposited on pyrolytic graphite electrodes by flash evaporation, and made available through the courtesy of Energy Conversion Devices, Inc.

2. Instantaneous Characteristics

The upper curve on Fig. 1 shows a set of results obtained with 6 microsecond pulses at intervals of several seconds. The curve remains unchanged when the pulse duration is reduced to the limit of convenient measurement, i. e. $\sim 0.5 \mu\text{sec}$, and no current creep is observable. This voltage-current relationship must thus be regarded as "instantaneous." Its nonlinearity must then have its origin in some high-speed process which, presumably, augments the free carrier concentration and cannot be ascribed to space charge accumulation. This also implies that the routine assumption of field uniformity is justified in this operational region, apart from small disturbances which are known to be associated with the contacts⁽⁶⁾.

3. Polarization Effects

The above characteristic may be compared with the voltage-current relationship (lower curve on Fig. 1) obtained by applying voltages in the form of continuous linear ramps, as shown in the insert. The corresponding con-

ductances are always lower than those obtained under pulses, which means that the differences cannot possibly arise from self-heating. The currents associated with ramp, though lower, flow for much longer times, which makes the total power dissipation enormously larger, as Fig. 2 shows. By going back and forth between ramp and pulse measurements, it can be ascertained that the internal modifications evidently caused by ramps are not of a permanent nature. The separation of the two voltage-current characteristics depends on the ramp gradient, as can be seen from Fig. 3a. The measured threshold voltages are also different, V_{TH} being ordinarily higher for ramp voltages, but lower for the slowest ramps. [However, the relationship between V_{TH} and ramp gradient has a maximum at ramp speeds of the order of 10^{-1} volts/ μ sec.]

The reduced conductances evidently arise from a slow internal polarization process, and this can be demonstrated as follows:

- (i) Ascending and descending ramps are expected to yield different currents (at the same voltage) and this is observed (Fig. 3b). Polarization in the presence of a high field affects most sensitively the conductance of the system as subsequently measured by a lower field.
- (ii) Short rectangular pulses may be superimposed upon the ramps at various epochs. They yield V-I characteristics intermediate between the two curves on Fig. 1. The corresponding loci of threshold points (for voltages of either polarity) are shown on Fig. 4. In general terms, a polarization which increases the system resistance for the prevailing direction of current flow, diminishes it when test voltages of opposite polarity are applied. In this way, the small amount of rectification originally observed can be increased or diminished, depending on the polarity of the ramp voltage. This can be demonstrated by superimposing non-switching

pulses and ramps, as shown in the Table.

Table I
Currents Associated with 6 μ sec Voltage Pulses Superimposed on a Slow Ramp. Typical Observations.

	Before Ramp	After 4.5 msec of a +ve 1.2 v/msec ramp
current at +12 volts	29 μ amp	26 μ amp
current at -12 volts	22 μ amp	30 μ amp

The relaxation time of the polarization effects can be assessed by applying a rectangular pulse at varying times after cessation of a ramp and monitoring the corresponding pulse characteristics. By an experiment of this type, the room-temperature relaxation time was found to be of the order of several milliseconds. This agrees roughly with the time constants ordinarily associated with negative current creep when constant pre-threshold voltages are applied. Negative current creep may thus be regarded as the direct consequence of this polarization.

It will be seen from Fig. 1 that the switching currents are the same for pulses and ramps, even though the corresponding threshold voltages are different. Whereas the pre-threshold characteristics are determined by the prevailing field, switching does not occur until a certain threshold current is reached. A similar observation has been made by Pryor⁽⁶⁾ in connection with experiments on the rectification aspects. It must evidently have an important bearing on the switching mechanism itself.

4. Space Charge Models

The experiments demonstrate internal polarization, but do not by

themselves indicate its nature or polarity. Free carrier polarization would have the consequence shown in Fig. 5a, polarization by injected and subsequently trapped carriers those shown in Fig. 5b. The first process leads to a field reduction in the interior; the second process leads to a field increase, if (and, of course, only if) it predominates over the free carrier and dielectric polarizations. Since the free carrier polarization needs, above all, free carriers, it will become increasingly prominent as the applied field is increased and the threshold voltage is approached. Since Fig. 5b implies a negative (effective) polarizability, it has been suggested as a model for the explanation of negative capacitance effects⁽⁷⁾. It also explains the negative current creep⁽⁶⁾ most readily, because the space-charge build-up is expected to impede the entry of further carriers. On the other hand, the negative current creep is always small, which means that the net (injection minus free carrier) space-charge build-up and the resulting field distortion must be small also.

Previous experiments⁽²⁾ suggested that a space-charge reversal occurs in the course of switching. The potential configuration corresponding to the ON-state (broken line) must be similar in character to that given by the full line on Fig. 5a, because the ON-state is virtually independent of film thickness. The profile is here drawn as symmetrical, but this is not actually a necessary or established feature. The essential feature is the field-free interior. It is thus plausible to conclude that the configuration in the pre-threshold regime should be as given by Fig. 5b. However, whereas switching, in a previously proposed model⁽⁷⁾, was ascribed to an overlap of the two space charges, this is now known to be incorrect. Among other things, the development of overlap during the switching delay time (e. g. up to 5 or 6 μsec) would imply substantial negative creep during that time, whereas it is here shown that space-charge formation takes much longer.

5. Discussion and Conclusions

The results show that scaling relationships should be established by means of short pulse measurements, avoiding signal forms which lead to polarization. The polarization process here described can evidently modify switch behavior, and does so under a variety of operational conditions, but is not itself an essential feature of the switching mechanism. Assume that a ramp voltage is applied and injected carrier polarization gradually established. As the threshold field is reached and the number of free carriers has suitably increased, free carrier polarization will begin to dominate, leading to the configuration of Fig. 5a. When a sufficient dipole has been created, the barrier [whether present on both sides or only on one, as recently suggested by van Roosbroeck⁽⁸⁾] becomes transparent to carriers and the ON-state is thereby established.

The model accounts, albeit qualitatively, for the principal performance features of switching systems. Conditions are, in a sense, more complicated when pulse, as opposed to ramp, voltages are applied, because the two types of polarization would thus go on simultaneously and tend to cancel. Which of them would 'win' would depend on detailed structural features. Correspondingly, there are in fact substantial variations from specimen to specimen, as regards the effect of voltage reversal on the switching delay time. When a threshold voltage pulse is applied and subsequently reversed before the end of the switching delay (t_D), the total delay is generally increased.

At low temperatures, the effect is always prominent⁽¹⁰⁾, at room temperature, it is prominent in some units (-up to 30% increase of t_D recently observed-) and much less in others^(9, 10). At higher temperatures, the effect disappears. Two questions arise: (a) how can the lengthening effect ever disappear, and (b) why is the current virtually constant during a simple switching delay t_D ? The lengthness effect can disappear if the prevailing free carrier

concentration is high enough, since that would enable the free carrier space charges to change polarity with great speed. The current during t_D is believed to be almost constant because the total resistance is controlled primarily by the barriers (rather than the bulk) during this particular phase of the events.

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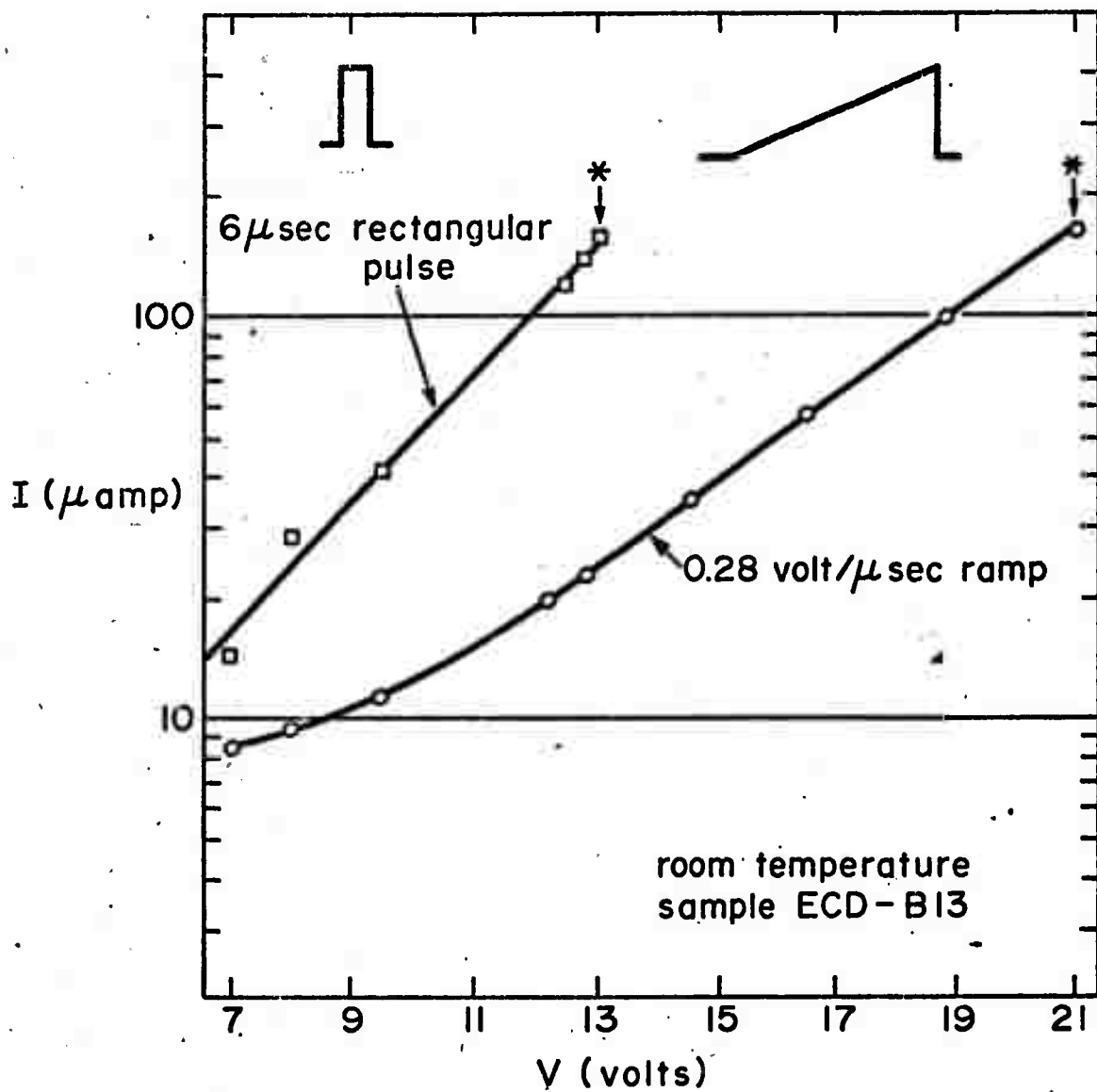


FIG. 1 V-I characteristics and switching under pulse and ramp conditions. Asterisk indicates threshold point.

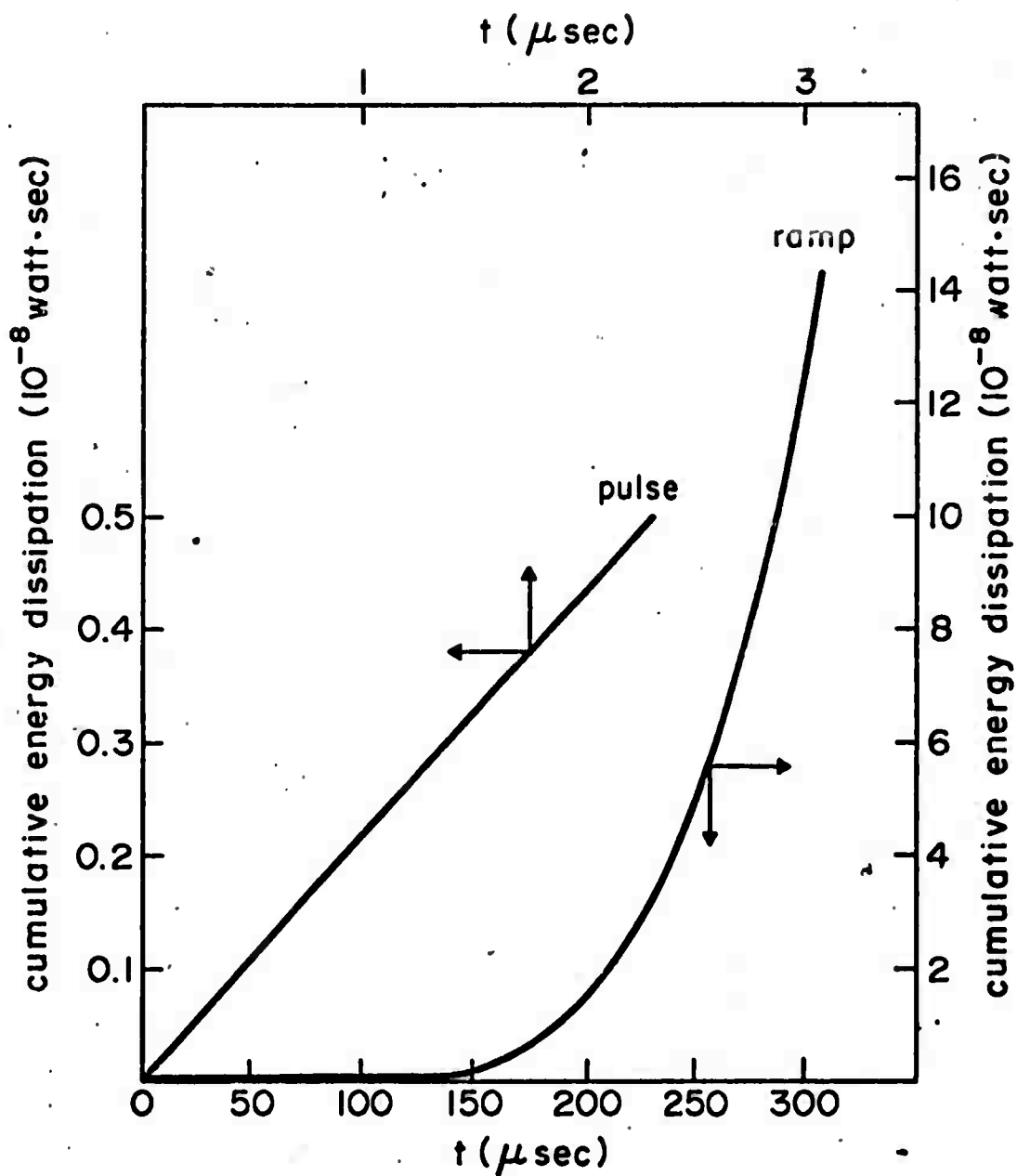


FIG. 2 Cumulative energy dissipation under typical pulse and ramp conditions.

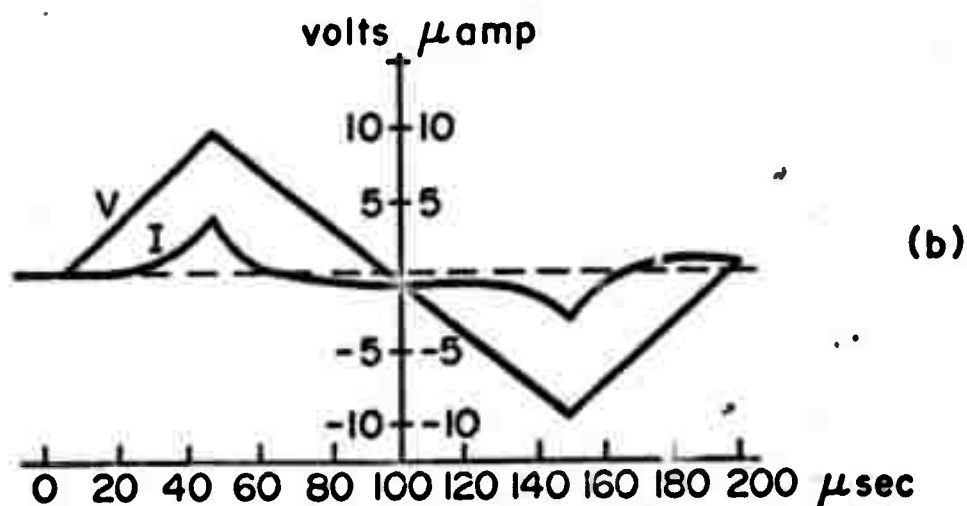
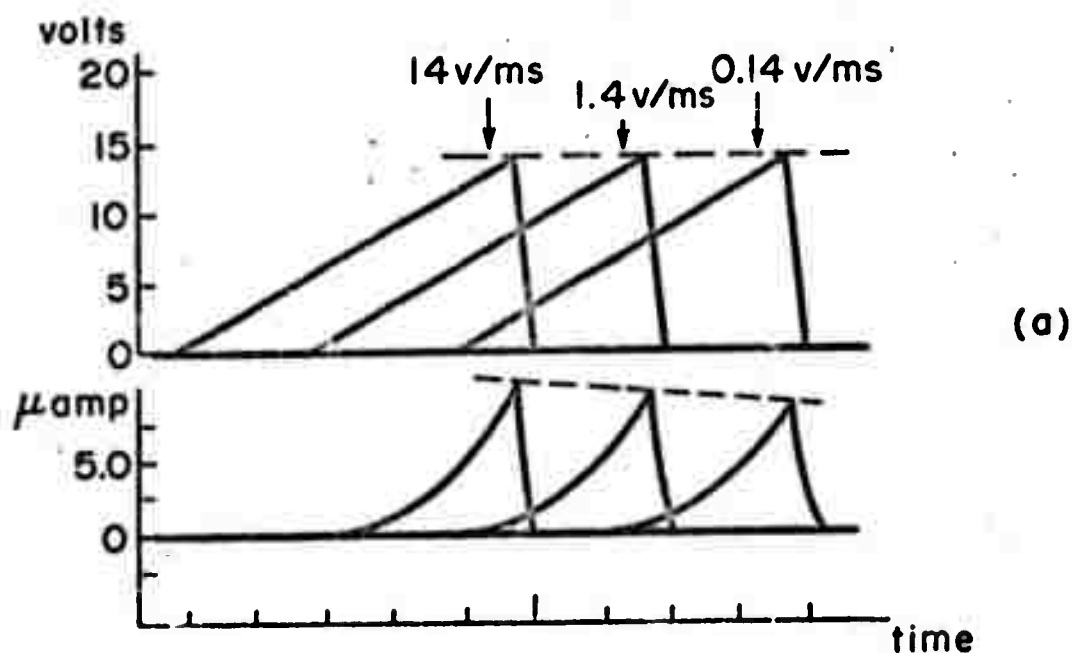


FIG. 3 Polarization effects under ramp conditions.

- (a) Dependence on ramp speed. Upper traces: three pre-threshold voltage ramp speeds (left to right: 14 V/ms, 1.4 V/ms, and 0.14 V/ms, respectively) displayed on varying time scales. Lower traces: the corresponding currents.
- (b) Current variations under linear ascending and descending voltage ramps. Horizontal time scale: 20 $\mu\text{sec}/\text{div}$. Vertical scale: 5 volts/div., 5 $\mu\text{amps}/\text{div}$.

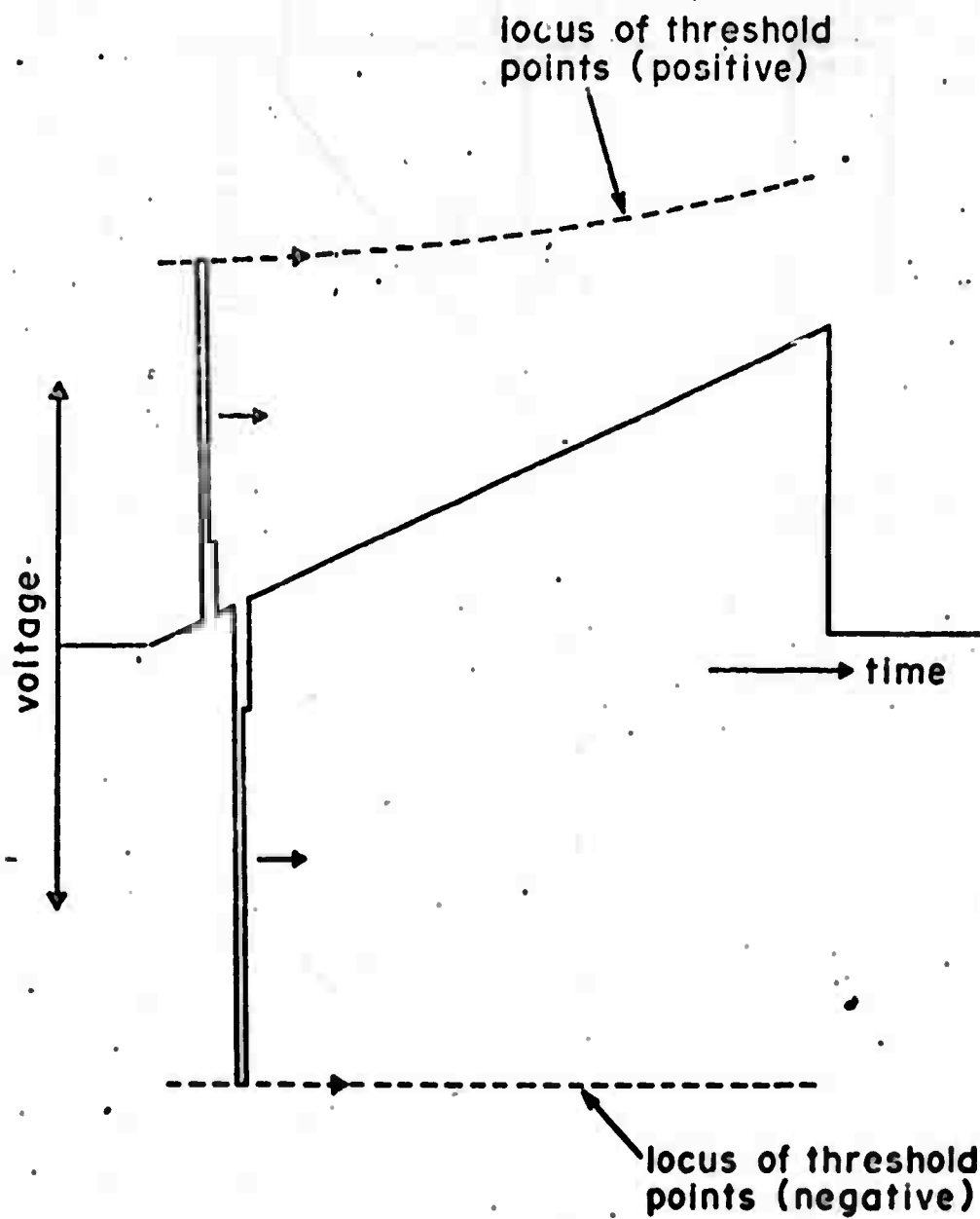


FIG. 4 Effect of voltage ramps on the threshold voltage. At high ramp speeds, the loci of threshold points are both horizontal.

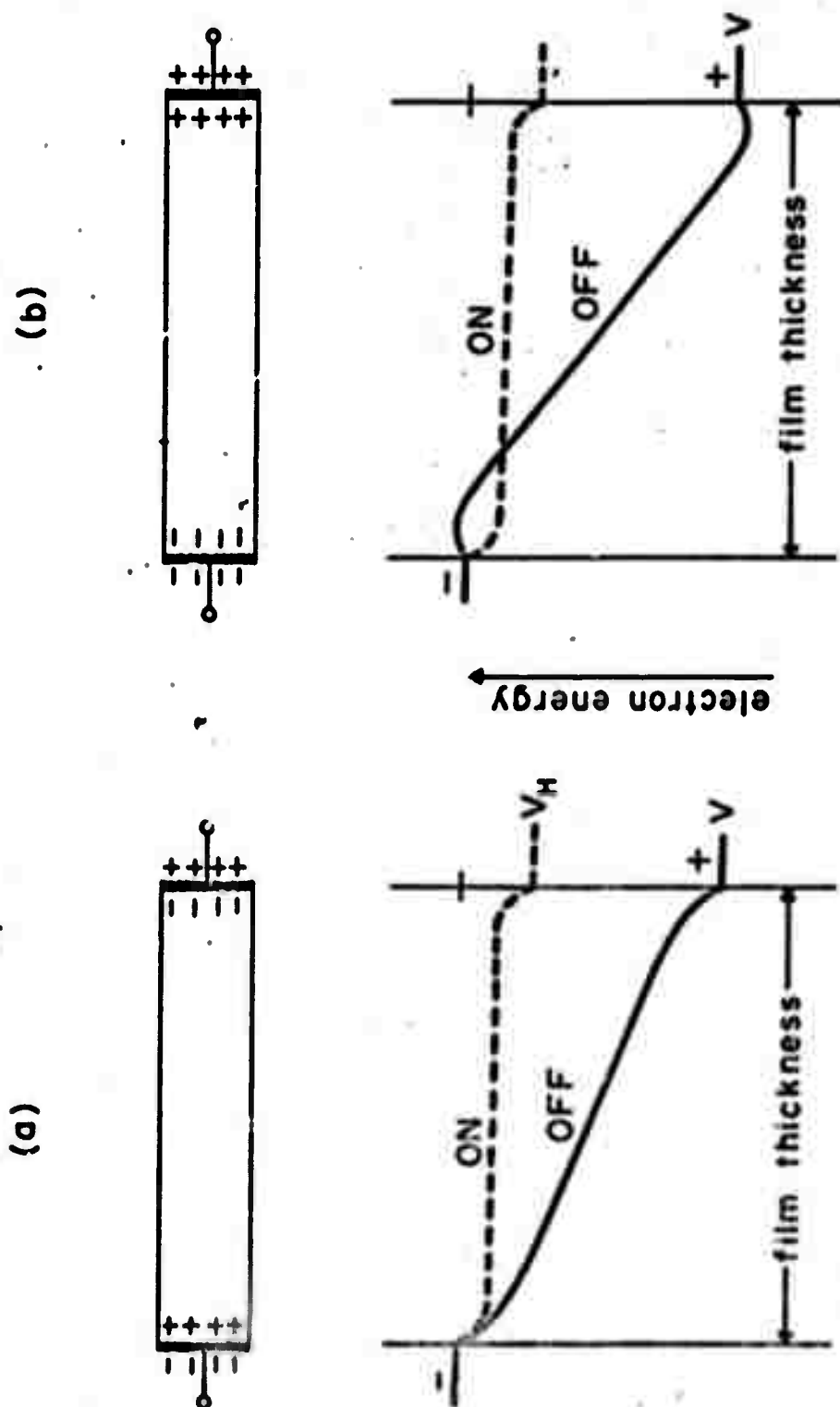


FIG. 5 Polarization models.

- (a) Free carrier (and dielectric) polarization.
- (b) Injected space charge polarization - for low pre-threshold voltages V applied; at higher voltages, there is likely to be an additional internal field distortion, arising from the field dependent conductivity.

Thermal and Non-thermal Processes in Threshold Switching

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ABSTRACT

The paper is concerned with thermal and non-thermal operating conditions of threshold switches made of multicomponent chalcogenide glass alloys $[\text{Te}_{40}\text{As}_{35}\text{Ge}_7\text{Si}_{18}]$. The observed current-time and frequency-delay relationships are shown to be inconsistent with thermal and electro-thermal models, and suggest electronic interpretations.

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Thermal and Non-thermal Processes in Threshold Switching

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Many early interpretations of threshold switching in amorphous semiconductors and especially in the multicomponent chalcogenide glasses relied on purely thermal models. These were based only on the heat balance equation, together with some assumption concerning the temperature dependence of the bulk electrical conductivity⁽¹⁻⁴⁾. It was soon found that such models could not account satisfactorily for even the primary switching characteristics, i. e. the voltage-current relationship. Electrical terms were therefore introduced, usually in the form of an electrical, field-dependent (for whatever cause) conductivity⁽⁵⁻⁸⁾. Such models ought to be called "electro-thermal", inasmuch as the electrical terms fulfill an essential function⁽⁹⁾, but they are often misleadingly referred to as "thermal" because of their formal reliance on the heat balance equation. Whether these terms will always take this particular form is doubtful, considering the increasing mass of evidence for contact and space-charge effects⁽¹⁰⁻¹³⁾, and corresponding theoretical expectations⁽¹⁴⁾. Moreover, electro-thermal models have not been successful in accounting for secondary switching characteristics, e. g. transient response⁽¹⁵⁾, light effects⁽¹¹⁾ and short-term memory^(10, 15). This note is intended to clarify various other aspects of the thermal-versus-nonthermal controversy, on the basis of recent observations.

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The question of whether threshold switching is based on a thermal mechanism is meaningful only at the minimum power level required for operation. Whatever electronic mechanism may be at work, it will always be possible to heat the system by applying a sufficiently high overvoltage and/or passing a sufficiently high ON-current through it (low series resistance). Demonstrations of heating⁽¹⁶⁾ or mass loss⁽¹⁷⁾ are not significant unless the minimum power requirement is observed. Similar cautions apply to the interpretation of electrical measurements on switching systems. The relationship between applied voltage V and switching delay t_D , for instance, is usually given in the form

$$t_D = t_{D0} \exp\left(-\frac{V}{V_0}\right) \quad V > V_{TH}$$

where t_{D0} and V_0 are empirical constants (see Fig. 1). It will be clear that such an equation cannot possibly refer to isothermal conditions throughout, since there is no way in which its validity can be established without applying high overvoltages. As the overvoltage $(V - V_{TH})$ increases, the temperature must increase also, no matter what type of mechanism is responsible for switching at $V \approx V_{TH}$. At what stage this increase is significant is not yet known, but a tentative conclusion may be reached from the fact that the curve on Fig. 1 appears to be composed of two distinctly different components. Not only is there an apparent discontinuity in the line joining mean values, but the statistical spread disappears rapidly at this point. That observations which appear to confirm thermal theory^(7, 18, 19) are occasionally made in the high overvoltage range is not at all surprising in the circumstances.

The next question concerns the prevailing mechanism in the low or zero overvoltage regime. Within that regime, the switching delay time t_D is subject to a statistical scatter at constant applied voltage^(20, 21). In the

ordinary way, the maximum delay times observed are in the region of 6 microseconds for film thicknesses of the order of $1\text{ }\mu\text{m}$. However, by controlling the applied voltage with sufficient accuracy, delay times up to 30 microseconds have recently been recorded, and fluctuations of t_D between that value and an absolute minimum of 3 microseconds. Even 30 microseconds may not represent an inherent maximum, but may reflect simply the residual instability and the noise of the pulse generator. For typical cases, the form of the voltage-time and current-time relationships is shown on Fig. 2. When the switching delay is very short, the significant features tend to be obscured by the inevitable capacitive spike, but for longer delays (e.g. $t_D > 1\text{ }\mu\text{sec}$) reliable observations are possible. When the applied voltage is close to the threshold voltage, the current is virtually constant throughout the switching delay. For delays exceeding about 10 microseconds, a very small amount of negative creep can be observed. For substantial overvoltages, on the other hand, there is pronounced positive creep before the instability point is reached. Whether it arises from continuous self-heating remains unproven, but it is in principle interpretable in this way. Moreover, the onset of this positive creep coincides with the discontinuity of the lines shown on Fig. 1 and thus with the disappearance of the statistical delay time spread. The absence of this positive creep for $V \approx V_{TH}$ means that some other mechanism must then prevail.

The delay time t_D has been interpreted in various ways. In the simplest models, for instance, it is the time necessary for the attainment of a certain minimum temperature which marks the onset of thermal instability. Simple heat-balance considerations^(4,8) which do not depend on detailed assumptions associate this instability point with a temperature rise of $10\text{-}20^\circ\text{C}$ above ambient at 300°C . Coward has shown⁽²²⁾ that the pre-

threshold ("OFF") current does not flow uniformly throughout the film volume as was at one time believed, but through a region which is permanently formed during the first (ever) switching event. He has also shown that the cross-section of this filament must be less than $1.2 \times 10^{-6} \text{ cm}^2$. This limit was inferred from considerations of minimum electrode size. By actual measurement, Cohen, Neale and Paskin⁽²³⁾ arrive at about $5 \times 10^{-8} \text{ cm}^2$ for switching units which approximate more closely to those here in use. Whether the ON-current after switching flows in a filament of the same thickness is a separate question with which these investigators were not concerned. We can, however, examine it here.

For materials (multicomponent chalcogenide glasses) ordinarily used for threshold switching, a temperature rise of $10\text{-}20^\circ\text{C}$ would lead to a current increase of 300 to 400% just before switching, if the current were flowing uniformly. In fact, the results show (see above) that whatever current rise there may be is less than 1% of the standing current. This, in turn, would lead to the conclusion that the ON-current and its corresponding temperature rise are confined to a filament within the modified region and of much smaller cross-section. With the above value for the cross-section of the modified region (CNP filament), this would imply a current filament of about $5 \times 10^{-10} \text{ cm}^2$ area (Fig. 3). Since the OFF-current before switching is of the order of $20 \text{ } \mu\text{amps}$, the corresponding OFF-current density would be about $4 \times 10^4 \text{ amps/cm}^2$. As the On-state is established, the total current increases by a factor of between 10^3 and 10^4 . Though the filament may later expand, the initial ON-current densities in that filament would thus be of the order of $4 \times 10^4 \text{ amps/cm}^2$. These are not, of course, realistic values, since the corresponding temperature rise would be enormous. Even if the current were not due solely to the temperature rise, such high current densities are too

large for filament stability. By way of comparison, the maximum stable current density in unsupported Al wires is 10^3 amps/cm² (24). Wires carrying current densities of the order of 10^5 amps/cm² begin to explode within picoseconds (25). It follows that the diameter of the pre-threshold filament must be considerably larger. It may, indeed, be as large as the Cohen-Neale-Paskin filament itself, in conflict with the widely held view that the onset of switching marks the onset of narrow filament formation. This, in turn, cannot be reconciled with the current constancy shown in Fig. 2. Moreover, if energy dissipation were the only or even the most essential criterion for switching, it would be difficult to understand how the energy requirements of successive switching events can differ by as much as a factor of 10! The most likely conclusion is that ON and OFF currents flow in filaments of about the same diameter. However, the ON-current densities which this implies, though 100 times smaller than the maximum current densities mentioned above, are still very high and very much in need of more detailed explanation.

In the operating regime $V \approx V_{TH}$, it is thus implausible to interpret t_D as a waiting period during which temperature rises continuously. An alternative interpretation (9, 26) suggests that the overall temperature rise is quite small and is over by the time the capacitive spike has terminated. For the rest of the time nothing happens, until some kind of fluctuation (whether thermal or electronic) lowers the local resistance somewhere within the electrode area. Such a fluctuation is sometimes referred to as a "nucleation", though the term, itself, adds no further clarity. As soon as the fluctuation occurs, the heat dissipation ceases to be uniform. Whatever the nature of the cause, a hot filament would form. The suggestion is that it does so in a time too short for observation on the present scale, i. e. $< 10^{-7}$ sec. Such a model could be reconciled with the virtual constancy of the current throughout t_D , but not with the observation of a minimum delay

time (e. g. 3 microseconds, in the case quoted above). If t_D is regarded as an isothermal waiting time, then its minimum value may be interpreted as the time during which a certain minimum charge flows into the system. During most switching events, of course, more than that minimum charge is passed. This is, indeed, what Haberland and co-workers⁽¹²⁾ have suggested on the basis of rather different observations. It has also been shown⁽²¹⁾ that the total resistance is slightly changed by each switching event. Each time a switch is "addressed" by a voltage pulse, it is therefore, in a sense, a slightly different system. Accordingly, the pre-switching current which flows during the time t_D is not quite the same from event to event, though the differences are too small to be realistically shown on Fig. 2. There is, however, correlation between pre-threshold resistance and t_D . The higher the resistance, the greater is t_D , as one would expect on the basis of a minimum charge hypothesis.

We are again led to the conclusion that the threshold process in the $V \approx V_{TH}$ regime is not convincingly interpretable on the basis of the conventional thermal and electro-thermal assumptions. A further supporting argument for concluding that other mechanisms must be at work can be derived from pulse experiments of the kind shown on Fig. 4. These demonstrate an increase of t_D with increasing pulse repetition frequency, whereas thermal models can envisage only a decrease. Relatively long-term non-thermal recovery processes must therefore be going on within the amorphous film⁽²⁶⁾. At room temperature, the effect is observable but smaller.

It should be noted that the total case against thermal models rests, besides, upon many observed forms of behavior which are outside the scope of the present discussion^(11, 12, 15).

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Figure Captions:

- FIG. 1 Typical relationships between delay time and applied voltage.
- FIG. 2 Schematic current-time and voltage-time relationship for threshold switching. Typical behaviour of chalcogenide glass systems.
- FIG. 3 Conducting paths in a chalcogenide glass switch.
CNP: Cohen, Neale and Paskin⁽²³⁾.
- FIG. 4 The time delay, t_D at two different pulse repetition frequencies. Ambient temp.: -79°C . Vertical scale: 10v/div, Horizontal scale: 1 $\mu\text{sec/div}$.
 $\text{Te}_{40}\text{As}_{35}\text{Ge}_7\text{Si}_{18}$ alloy.

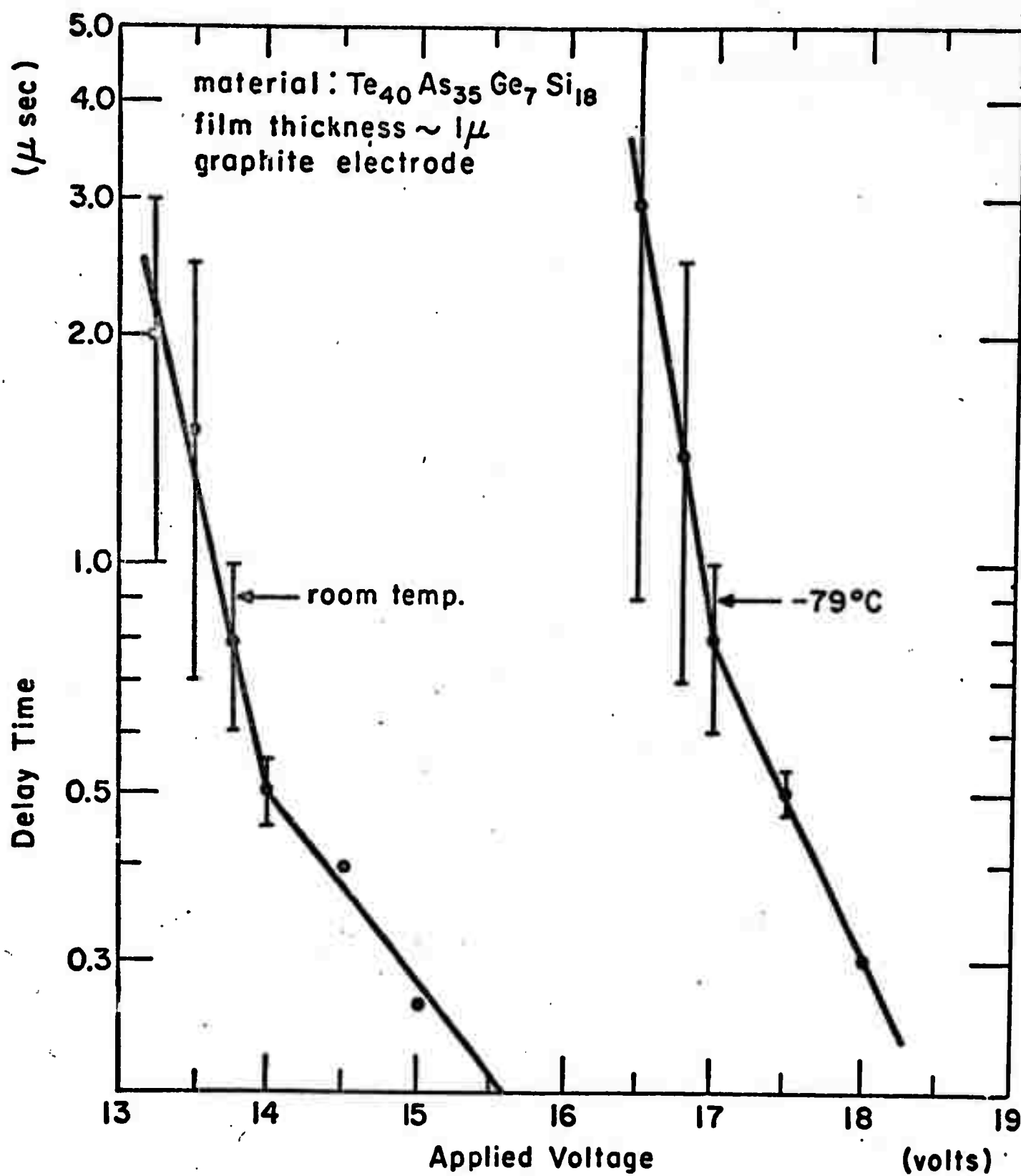


FIG. 1

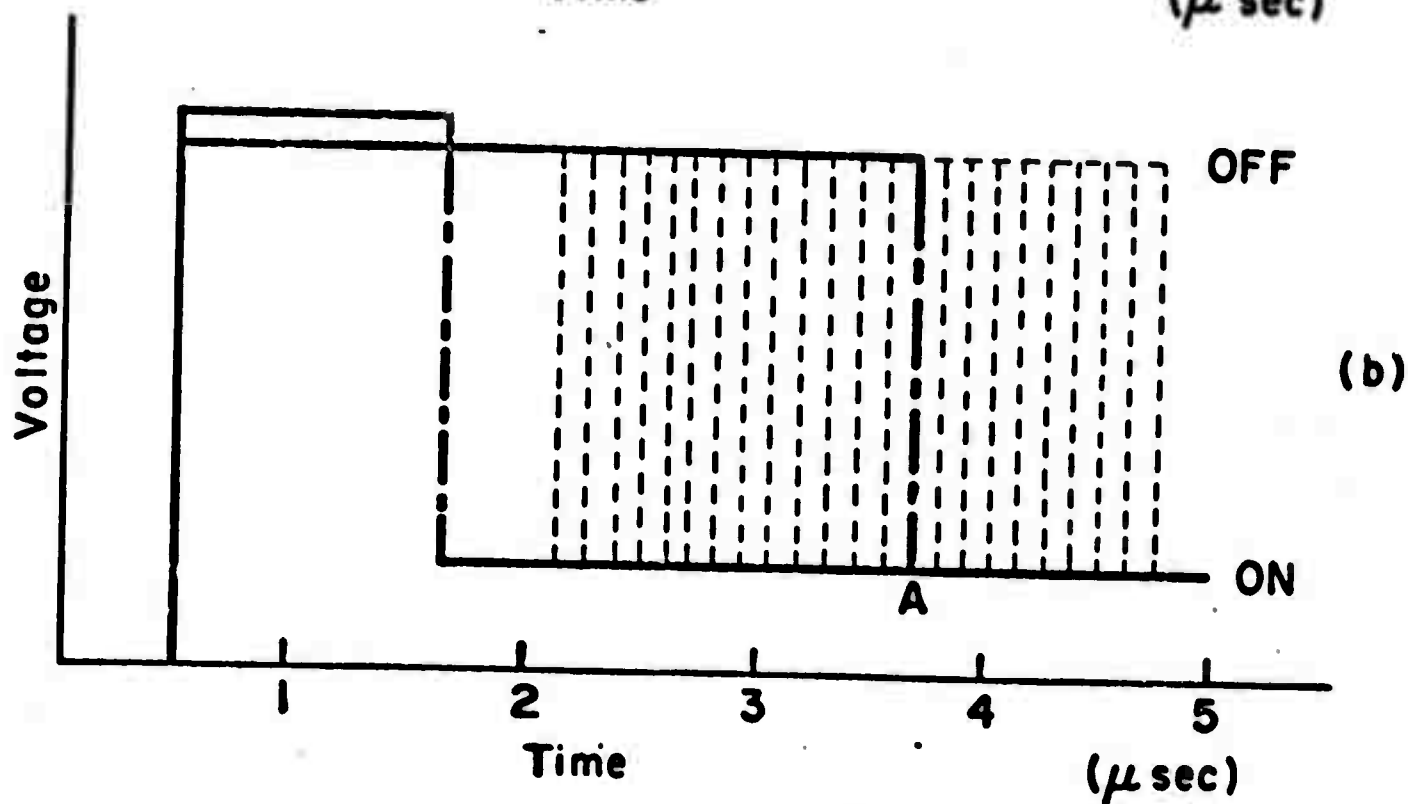
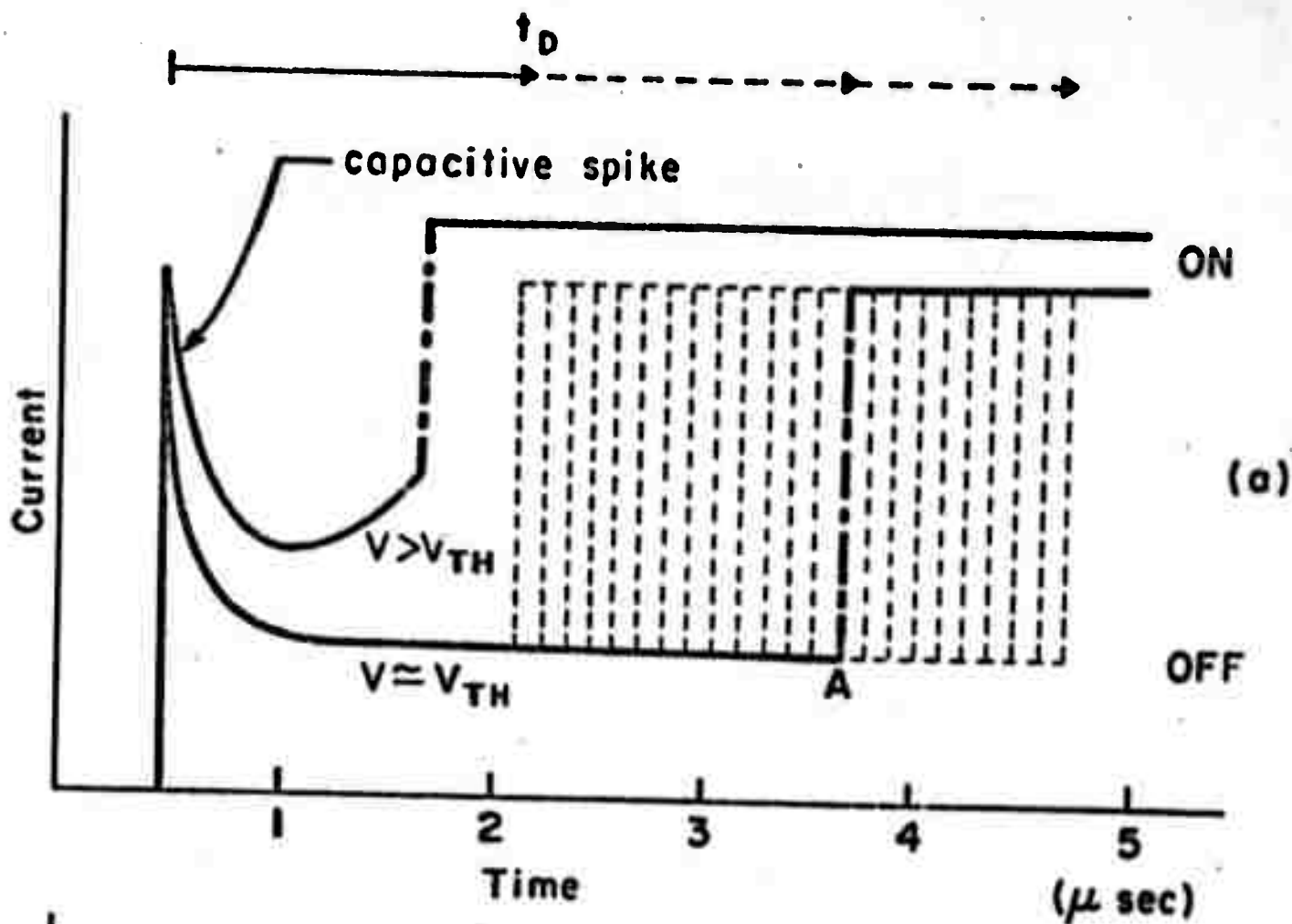
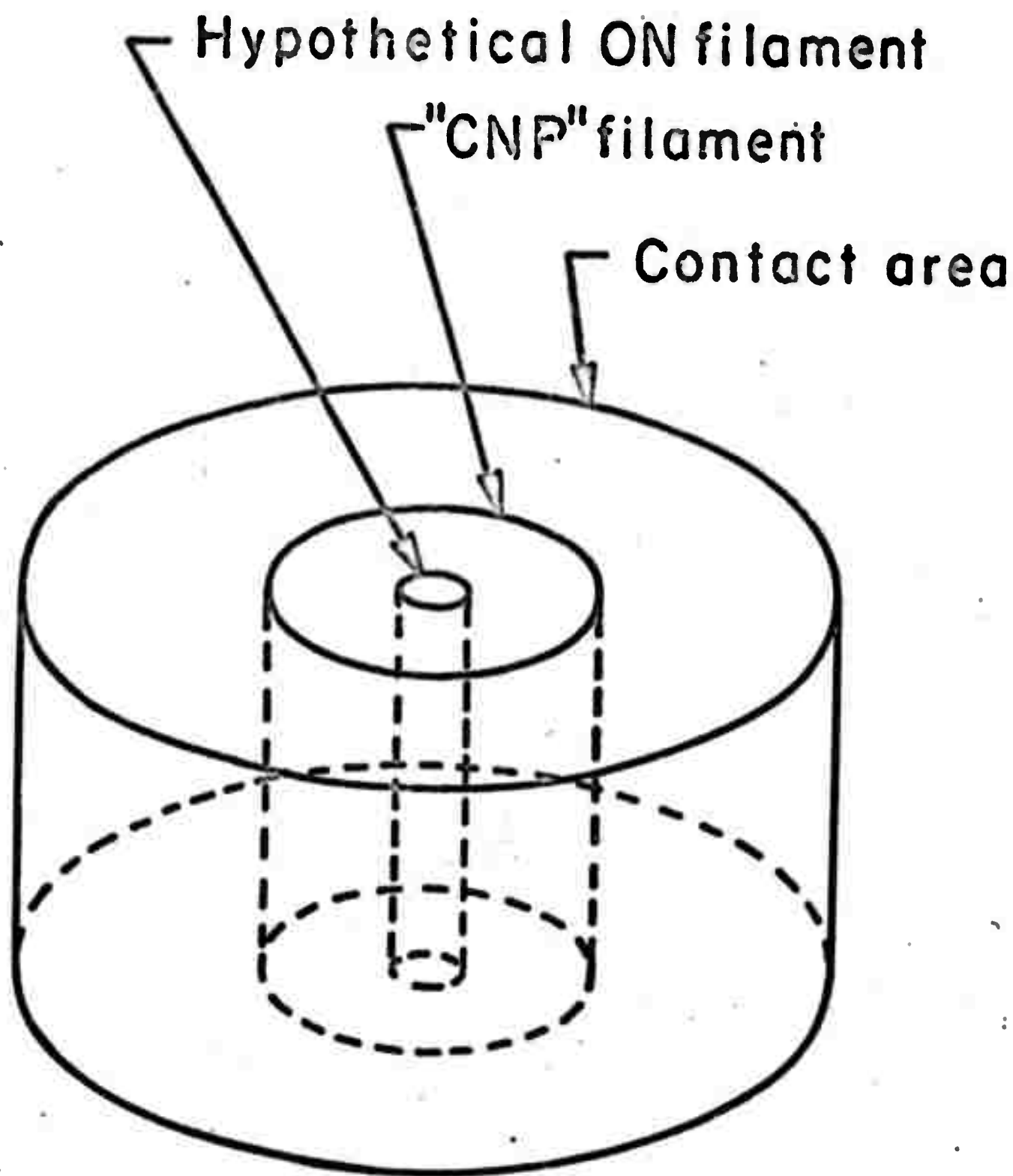


FIG. 2



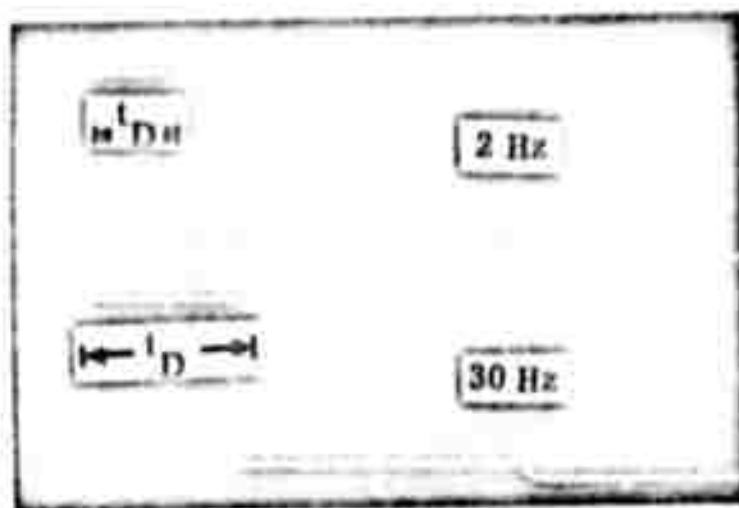


FIG. 4. The time delay, t_D at two different pulse repetition frequencies. Ambient temp.: -79°C . Vertical scale: 10v/div , Horizontal scale: $1\mu\text{sec/div}$.

Behavior of Amorphous Semiconductor Films Between
Asymmetric Electrodes

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ABSTRACT:

The paper describes switching operations made on chalcogenide glass films deposited on germanium substrates, and shows that they cannot be accounted for by any simple rectifier-and-switch-in-series model. The germanium-glass interface evidently plays a special role in determining switch behavior as far as (a) voltage-current relationships, and (b) resistance-time relationships are concerned.

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1. Introduction

The interpretation of switching phenomena in amorphous semiconductor films and particularly in the multicomponent chalcogenide glass alloys depends critically on the role assigned to the electrode interfaces. The first purely thermal models advanced (1-5) and even the more modern electro-thermal models (6-8) assign no such role, in harmony with the practical experience that the primary switching characteristic (i. e. the voltage-current relationship) is not sensitively dependent on the electrodes, as long as plausibly inert materials (e. g. graphite, tungsten, molybdenum) are used. However, the significance of this observation is in doubt, because important electrode effects have been noted in other contexts, e. g. by Altunyan and Stafeev (9), by Pryor, Henisch and Vendura (10, 11), and by Wey and Fritzsche (12). In one particular set of experiments (11), chalcogenide glass films applied to crystalline germanium surfaces and locally tested by means of graphite or tungsten point constants showed asymmetric switching characteristics, the asymmetry being reversed for n-type and p-type substrates. Because the interpretation of such experiments has an important bearing on our view of the switching mechanism, the nature of these observations

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is in need of more detailed examination.

During electrical tests on systems of the kind shown in Fig. 1a, the germanium and the glass appear inevitably in series. When the glass resistance dominates, as it does before the threshold voltage is reached, the V-I characteristic will reflect simply the OFF-state of the film. It should show some rectification in principle, but the asymmetry may not in fact be prominent enough to be observed. When the voltage across the glass is high enough, the film will threshold switch and go into the low resistance ON-state. If that state had zero resistance, the observed characteristic would be simply that of a germanium diode. Since the ON-state resistance is actually of the order of 100Ω , the observed characteristics are expected to be slightly different. The difference would show itself mostly in the forward direction of the germanium diode, as Fig. 1b demonstrates. For p-type substrates, the situation would be similar, except for the polarity reversal. No conclusions can be drawn as regards the switching mechanism, as long as the observed characteristics of the series combination conform to this pattern. Conversely, conclusions can be drawn if significant departures are observed which contradict the assumptions of simple, non-interacting series-connection. Such departures are described below.

The above comments are concerned only with the addition of the germanium V-I characteristics to the two limiting states of the glass film: ON and OFF. In addition, it is of interest to examine the voltage-time and current-time relationships which govern the interchange. Because the response of germanium diodes is extremely fast, the simple series connection of a threshold switch and a non-interacting diode is not expected to affect the switching time relationships. Conversely, it must be concluded from such effects (as described below) that some form of

interaction is taking place and that, accordingly, interface parameters play a significant role in switching.

The experiments were carried out on flash-evaporated films of $\text{Te}_{40}\text{As}_{35}\text{Ge}_7\text{Si}_{18}$ [bulk material supplied by Energy Conversion Devices, Inc.]. The germanium substrates (n-type, $40\Omega\text{cm}$, and $12\ \mu\text{sec}$ lifetime, p-type $11\Omega\text{cm}$, and $5\text{-}10\ \mu\text{sec}$ lifetime) were polished and etched. The corresponding voltage-current characteristics were generally of the type shown in Fig. 2 with, however, substantial variations from point to point. Some points do not show stable switching at all; others exhibit a double switching process with different time relationships at each stage. There is as yet no clear understanding of the local variations; electron microprobe tests have shown that they are not associated with major fluctuations of composition; micropitting of the surface may be responsible. The account given below concentrates on the widely observed features, to the exclusion of the more rarely encountered variants.

2. Evidence of Interaction

Evidence of interaction between the germanium electrode and the amorphous film may be derived from the following features of the voltage-current characteristics.

- (a) The holding voltage, as derived by extrapolation of the ON-state in the third quadrant is shown on Fig. 2 to be about 4 volts. However, variations between 2 and 8 volts have been observed (10) during tests on different switches. There is no way in which such high values can arise from any simple series connection between an ovonic switch and a rectifying contact. Tests on films simultaneously deposited on pyrolytic graphite substrates yielded consistent (and symmetrical) holding volt-

ages of 1.5 to 2 volts, and the rectifying characteristics of a typical Ge-graphite contact is also shown (broken line).

- (b) In some instances, the ON-state in the third quadrant is far more light sensitive than the measured forward characteristic of the germanium rectifier system by itself.
- (c) The minimum holding currents in the first and third quadrants are seen to be different (Fig. 3), in contrast to the behavior of normal ovonic switches with symmetrical graphite electrodes. This is not by itself proof of interaction, since it is known that asymmetric loading can produce ^{some} such result. However, one of the minimum holding currents (Fig. 3b) is ^{sometimes} ~~seen to be~~ below the threshold current, and that is an unexpected feature.

3. Time Relationships

For typical films of 0.2 μm thickness on Ge substrates, Fig. 4 shows frequently encountered forms of the voltage-time relationships. It can be noted that these are entirely different for the two directions of current flow. There is therefore no question of simple scaling, the only process which a non-interacting rectifier would be capable of superimposing on switching behavior. The results leave no doubt about the fact that the differences are associated with the nature of the electrode interfaces. The Ge-glass interface, in particular, cannot be expected to be an equally good electron and hole emitter; its injection efficiency is bound to depend on the direction of the prevailing barrier field. Because the band gap in Ge is smaller than the mobility gap in the glass, a small barrier to electron flow should exist when the Ge is negative with respect to the glass, whereas there should be no barrier to hole flow when it

is positive. Hardly anything is known about the detailed nature of the interface but, in qualitative terms, some such asymmetry is entirely expected. The slow voltage drop (implying a conductance increase) on Fig. 4b is reminiscent of experiments with optically injected carriers (12), the time required to reach the steady state being interpreted as the time required for injected carriers to penetrate the entire film thickness.

The fact that the two mechanisms of current flow are different in the two directions is also shown by their response to illumination. This is illustrated by the dotted lines on Fig. 4a for a film on an n-type Ge substrate. The low resistance state in the negative direction is independent of light, and of the applied external voltage. In view of this, and because the low resistance state is reached sooner when the applied voltage is higher, this condition corresponds most closely to the ON-state of conventional threshold switches. For amorphous layers on p-type Ge substrates, the results are somewhat similar, but with reversed polarities. However, no light effect was observed for negative applied voltages; for positive voltages the resistance was light dependent (Fig. 2b) throughout.

There is another important respect in which the behavior of symmetrical and asymmetric systems differs. For conventional (symmetrical) threshold switches, it is well known (13, 14) that a switching operation reduces the threshold voltage experienced by a subsequent switching process, if the time interval is small enough, e.g. of the order of 1 μ sec for film thickness of the order of 1 μ m. The threshold switch "remembers" a previous operation. From opposing viewpoints it has been argued that this temporary memory is electronic in nature or, alternatively, that it is purely thermal. Figure 5 gives results of a "rare double-pulse experiment"

carried out on an asymmetric n-type system as described above. In the upper trace, two equal voltage pulses are about 10 microseconds apart, and each exhibits switching (in the manner shown on Fig. 4a). When the pulses are moved together, without change of applied voltage, the second pulse ceases to switch. There is a threshold voltage increase towards smaller time intervals, instead of the decrease ordinarily observed. This trend persists over at least 9 microseconds, down to 0.5 microsecond (Fig. 5b), the limit of observation for the test circuit used. The increase is found for a substantial number of contact points but not for all of them; some show the conventional form of behavior. What happens at shorter time intervals is not yet known. Meanwhile, it is important to note that a threshold voltage increase cannot be associated with heating, and must therefore arise from electrical (and, in all probability, electronic) causes. The fact that such an upward trend can exist (for whatever reason) also means that the frequency cut-off presently associated with threshold switches is not necessarily an inherent and permanent feature.

Acknowledgements

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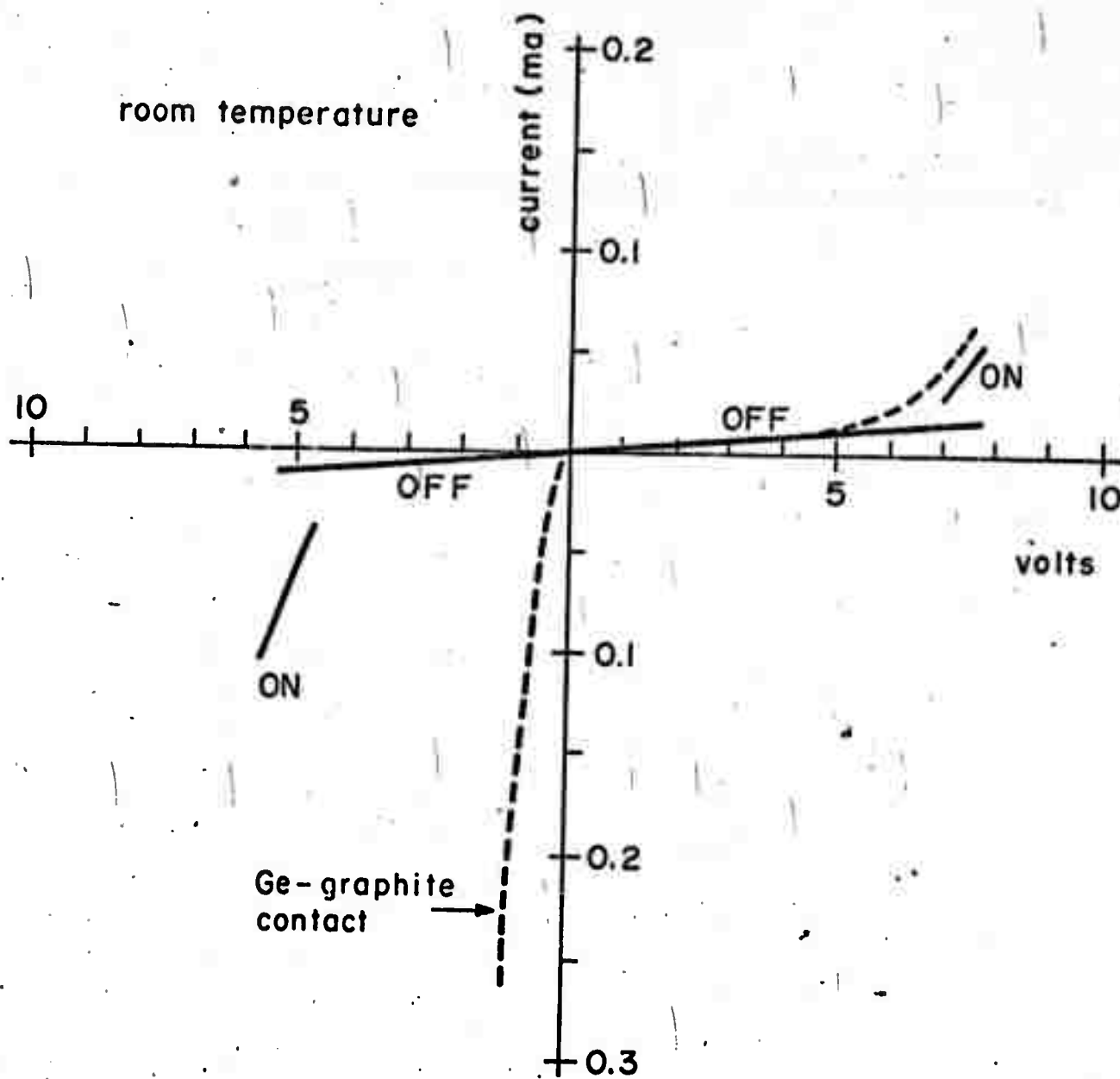


FIG. 2 Switching systems with asymmetric contacts; dynamically tri-stable voltage-current characteristics.

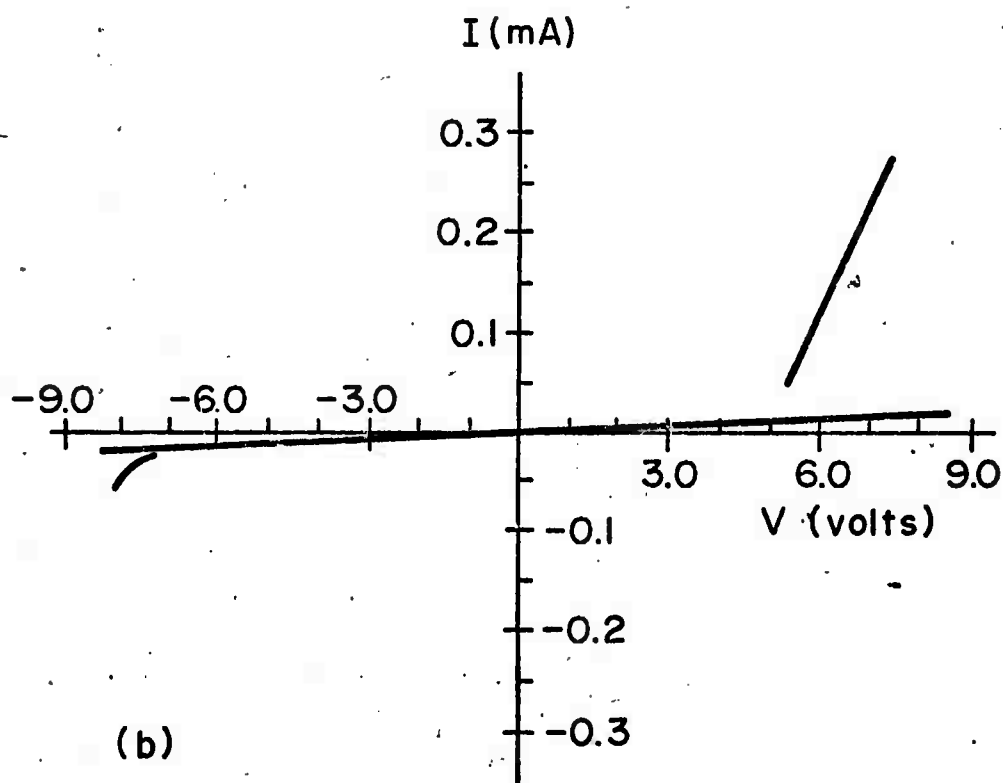
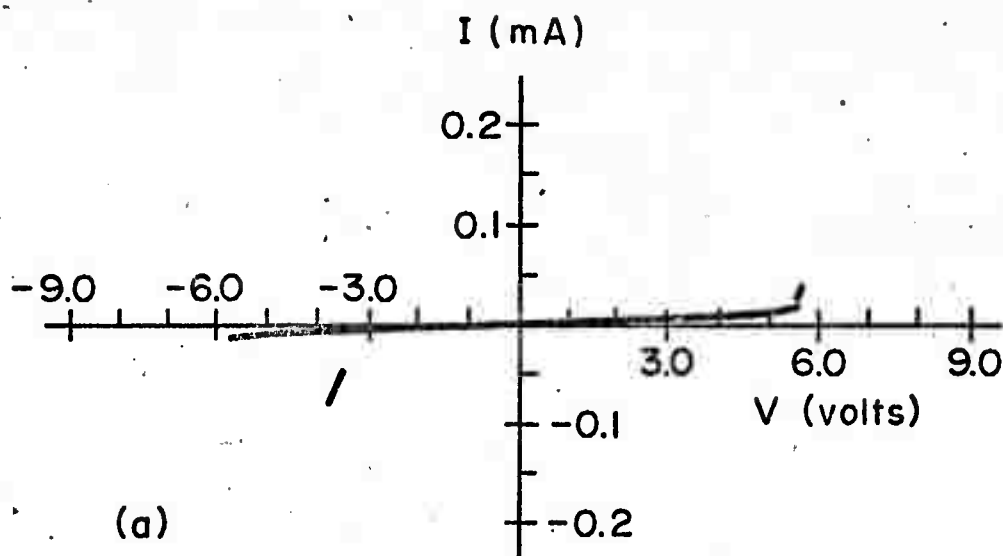
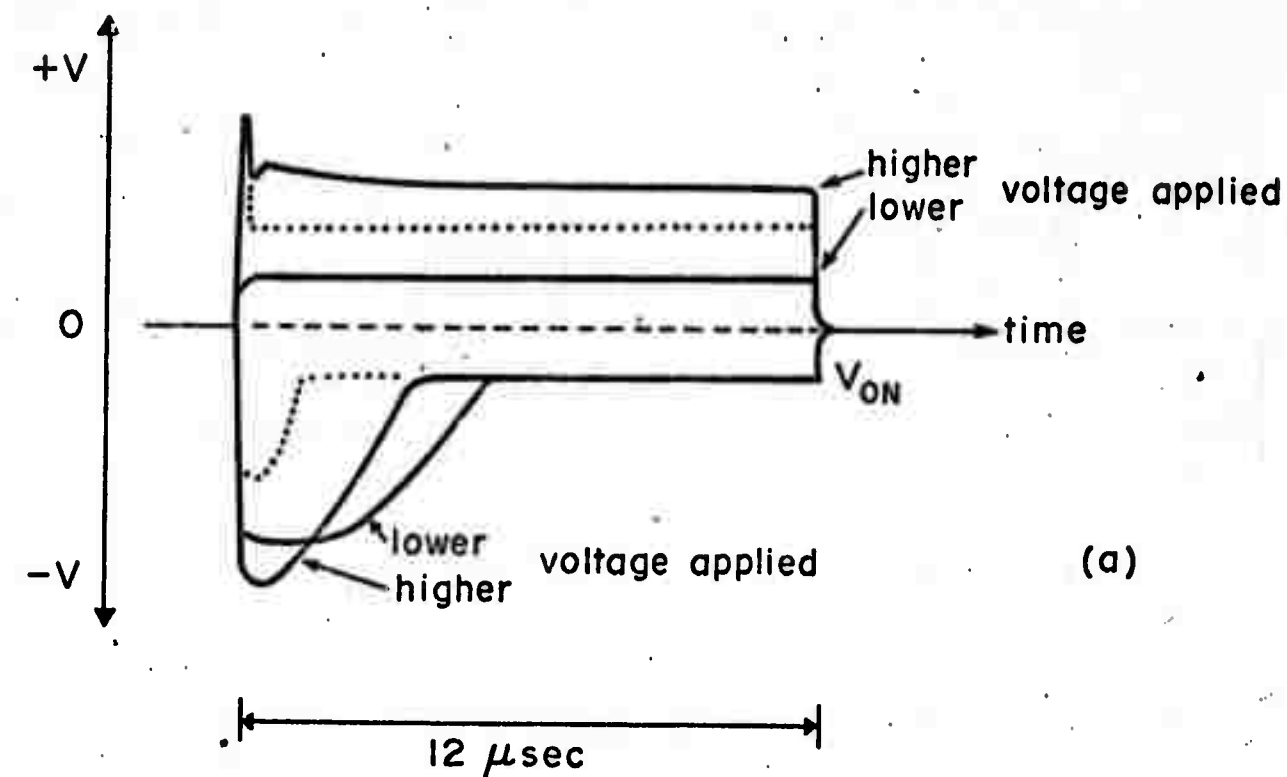
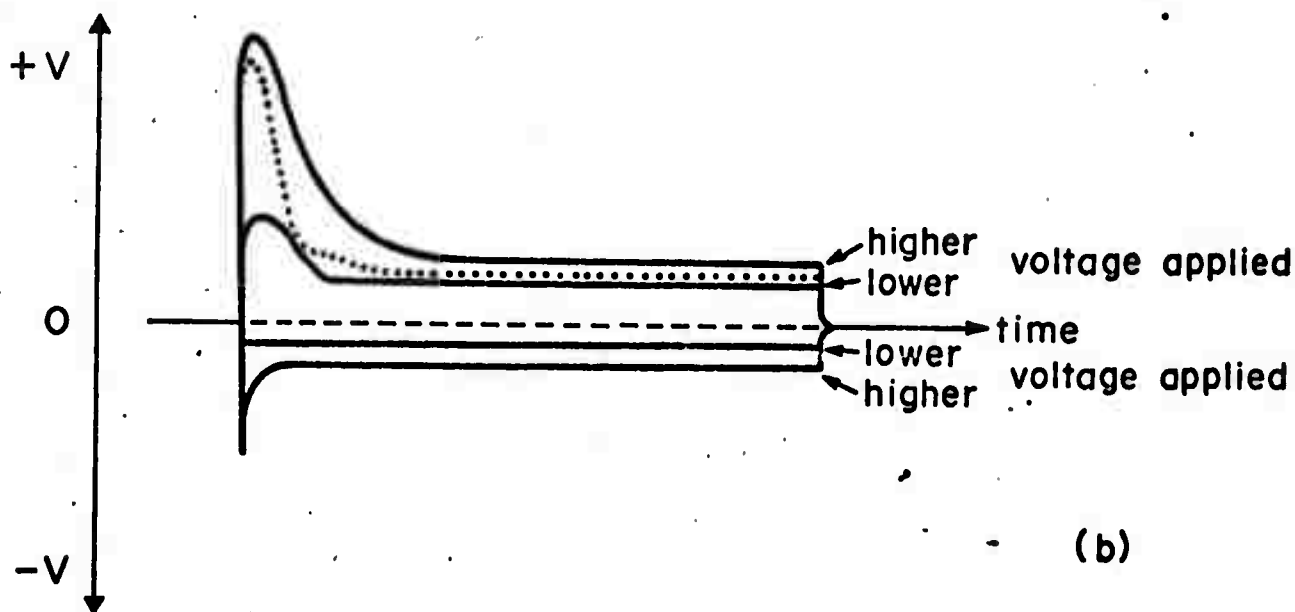


FIG. 3 Oscilloscope traces of V-I characteristics obtained on systems as shown on Fig. 1a.
 (a) asymmetric minimum holding currents (n-type substrate).
 (b) minimum holding current lower than threshold current (p-type substrate).



(a)



(b)

FIG. 4 Voltage-time relationships for switching systems with one tungsten and one germanium electrode.

(a) n-type Ge.

(b) p-type Ge.

Positive direction corresponds to polarity of the tungsten contact. Dotted lines denote characteristics under illumination.

($\text{Te}_{40}\text{As}_{35}\text{Ge}_7\text{Si}_{18}$; film thickness $\sim 0.2 \mu\text{m}$.)

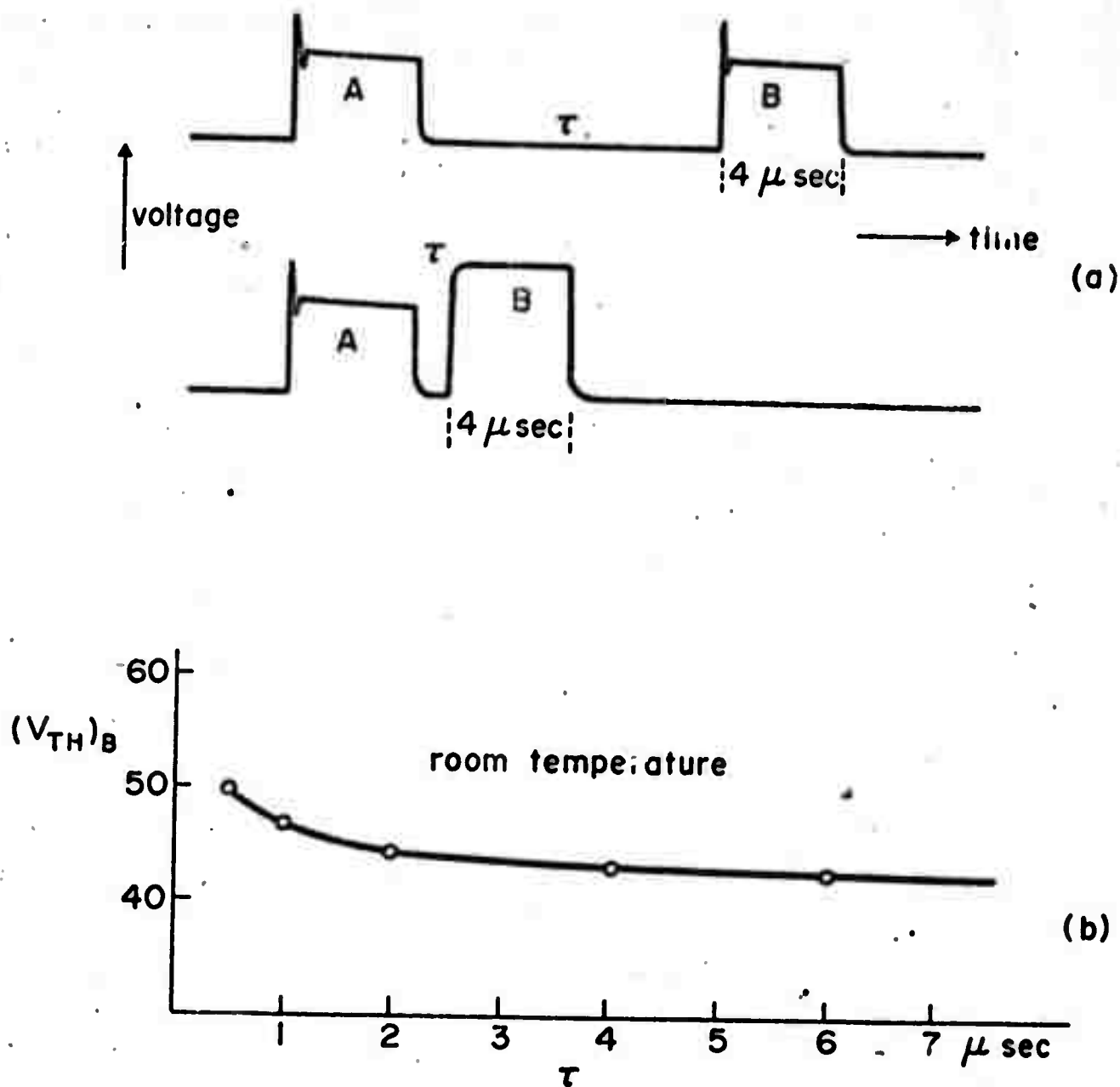


FIG. 5 Double pulse experiments on switching systems with asymmetric contacts (tungsten point contact, n-type Ge substrate).
 (a) upper trace: A and B pulses far apart; both pulses switch.
 lower trace: A and B pulses close together, with same external voltage applied; B pulse does not switch.
 (b) the $V_{TH}(B)$ - τ relationship for such a contact point.
 Pulse pair repetition frequency: 50 per sec.
 $\text{Te}_{40}\text{As}_{35}\text{Ge}_7\text{Si}_{18}$ film thickness: $\approx 0.2 \mu\text{m}$.

Relaxation Processes in the Chalcogenide GlassThreshold Switches

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ABSTRACT

The paper is concerned with thermal and non-thermal relaxation processes. The free carrier lifetime, as assessed from the time-decay of the ON-state condition, is shown to be of the order of 0.1 microsecond. The short-term memory exhibited by threshold switches is interpreted in terms of this free carrier decay. It is shown that sequential switch operation is, additionally, influenced by the dielectric relaxation time which governs space charge decay. There is also a (very small) thermal contribution to switch recovery. It depends on the initial temperature distribution and thus on the duration of the preceding ON-state.

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Relaxation Processes in the Chalcogenide Glass Threshold Switches

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Introduction

It is known that the behavior of chalcogenide glass threshold switches depends on the time interval between the addressing pulses. When two successive pulses are applied to a switch, the threshold voltage of the second pulse is reduced as the interval between the pulses shortens. The general form of behavior is shown schematically in Fig. 1a. Two regions are of special interest in the present context; that of very small and that of substantial time intervals τ . If the separation of the two pulses is very short, say 0.1 μsec , then the ON-state can be restored without further delay, i.e. without necessitating a renewed switching process⁽¹⁾. Within such a time interval, the behavior is insensitive to the ambient temperature⁽²⁾. When the switch is addressed with a periodic switching pulse of much lower frequency, the switching delay time (t_D) increases as the frequency of the pulse increases⁽³⁾, as shown on Fig. 1b. If it is clear that, if thermal considerations alone were to prevail, the opposite behavior would be expected. The delay time also increases when the total width of the addressing pulse is increased. Such a relationship is shown on Fig. 2, for a typical threshold switch** made of $\text{Te}_{40}\text{As}_{35}\text{Ge}_7\text{Si}_{18}$, using graphite electrodes (film thickness $\approx 1\mu$). These effects are most readily observed at lower temperatures. It is also known⁽⁴⁾

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**supplied by Energy Conversion Devices, Inc.

that the switch is slightly more conductive after an ON-state than before. At room temperature, the additional conductance decays in a time of the order of minutes. This is accompanied by a gradual recovery of the threshold voltage, as shown by the slight slope of the $V_{TH} \sim \tau$ relationship on Fig. 1a. Results for time intervals τ of the order of minutes are discussed in this paper. In fact, albeit at a very low rate, the recovery process continues for days. During such a period of time, the threshold voltage may show a further increase by a few (e. g. 6) percent. Considering the time factor involved, this last process is likely to be associated with the structural stabilization of the glass, as commonly found⁽⁵⁾. The present work is not concerned with it.

The fact that t_D increases with increasing frequency for a constant applied voltage appears inconsistent with the behavior of the threshold voltage on Fig. 1a and the known (fixed frequency) relationship between V_{TH} and t_D . It is thus necessary to investigate the process in which the chalcogenide glass switch relaxes after an ON-state in greater detail. The results of the present work (see below) show that the switch goes through three distinctive relaxation processes which are associated with (1) the disequilibrium of carriers in the ON-state and their subsequent recombination during the following OFF-state; (2) space charge decays through dielectric relaxation, and (3) cooling. It is found that these processes are consistent with the Land model of amorphous semiconductors, as proposed by Mott⁽⁶⁾, Cohen, Fritzsche and Ovshinsky⁽⁷⁾ and also with the transport considerations of van Roosbroeck⁽⁸⁾.

The ON-state of the switch, interpreted as a double injection system by Mott⁽⁹⁾, Henisch et al⁽¹⁰⁾, is briefly described as follows. The potential drops are mainly at the electrode interfaces (see insert, Fig. 4). This conclusion is based on the fact that the ON-state is almost independent of film thickness. The voltage drop occurs, presumably across space charge regions.

To sustain the space charges (and thus the ON-state), a minimum holding current, I_{MH} , is required. In the interior of the film, the conductivity must be very high, implying a large excess of free carrier concentration under conditions of neutrality. When the ON-state is terminated, free carriers and space charges must decay but not, of course, at the same rate. In a relaxation semiconductor^(8, 11), the space charge decay is governed by the dielectric relaxation time. The observations described below permit the evaluation of the free carrier lifetime and lead also to estimates of the ON-state filament temperature.

The Free Carrier Lifetime (τ_f)

A pulse sequence with which ON-state interruptions can be conveniently explored is shown by the Insert in Fig. 3 (right center). If the ON-state is to be restored without renewed switching, a total interruption time t_g must not exceed a certain maximum value, namely $t_g(\text{max})$. Henisch, Pryor and Vendura⁽¹⁾ have shown that $t_g(\text{max})$ depends on the prevailing ON-current, as given by the Insert. These curves have been schematically extrapolated to $t_g(\text{max}) = 0$, for which the intercept should yield I_{MH} , the minimum holding current. Its value, when independently measured under pulse conditions, varies somewhat from specimen to specimen, averaging about 1 mA for the material and film thickness in question. The above extrapolation is in excellent agreement with this value.

One may assume that the free carrier concentration corresponding to I_{ON} decays exponentially with time in accordance with

$$N = N_{ON} \exp(-t/\tau_f) \quad (1)$$

and reaches the value N_{MH} , corresponding to I_{MH} in time $t_g(\text{max})$. N stands for a total effective concentration, without reference to its composition as between electrons and holes, and t is the time since the cessation of the ON-state.

When the points corresponding to $[I_{ON}, t = 0]$ and $[I_{MH}, t = t_s(\max)]$ are entered into Fig. 3, the corresponding slopes are seen to be identical at a given temperature. From this common slope, the free carrier lifetime at room temperature is found to be $0.13 \mu\text{sec}$, and τ_f is evidently independent of I_{ON} within the range measured. At -77°C , τ_f is reduced to about $0.10 \mu\text{sec}$. Thus, the lifetime appears fairly insensitive to changes of ambient temperature, as one would expect in an amorphous semiconductor, because the Fermi level remains nearly at the center of the mobility gap. In this respect, amorphous semiconductors differ from the crystalline variety⁽¹²⁾.

On the basis of the present lifetime estimate, Fig. 1a can now be re-interpreted. In a previous paper, Henisch and Pryor⁽¹³⁾ regarded the knee τ_k as a time necessary for charge release from traps. However, such a mechanism would imply a steep temperature dependence of τ_k which is not in fact observed⁽¹⁶⁾. We see now that τ_k exceeds τ_f by only a small factor of 7 or 8. τ_k is thus a reasonable time for the total disappearance of the free carriers. The lack of temperature dependence is then in agreement with the results given above. Space charges accommodated in traps also play a role, but evidently not an important one⁽⁹⁾ in the ON-state. We know this also from the speed with which the current can be reversed while the switch remains in an ON-state⁽¹⁾. The decay constant of the space charges is much longer, as shown below.

The Dielectric Relaxation Time (τ_d)

At the termination of the ON-state, the switch is still polarized by the space charges. The resulting field will decay according to $E_0 \exp(-t/\tau_d)$, where $\tau_d = \epsilon/\sigma$, since the materials concerned are relaxation type semiconductors, as defined by van Roosbroeck⁽¹¹⁾. This means that $\tau_d > \tau_f$. In the presence of the ON-voltage (V_{ON}), E_0 acts as a screening field between the

space charge regions. Because the space charges in the ON-state must be close to the electrodes, E_0 implies a screening voltage $V_0 = E_0 \cdot d$ where d is the film thickness.

In the normal way, the switching delay t_D depends on the applied voltage in accordance with the empirical relationship

$$t_D = t_{D0} \exp(-V/V_c) \quad (2)$$

which applies to very rare pulses, and which for $V \approx V_{TH}$ may be considered to correspond to isothermal conditions. When, after a long rest period, two identical switching pulses are applied to the system in rapid succession, the effective internal field created by the second pulse will be smaller, due to the screening field remaining after the first. The effective applied voltage would thus be $V - V_0 \exp(-t/\tau_d)$, which, in conjunction with eqn. (2), implies a modified time delay t'_D for the second switching process given by

$$\log(t'_D/t_D) = \frac{V_0}{V_c} \exp(-t/\tau_d). \quad (3)$$

which can be tested experimentally. Figure 4 shows $\tau_d = 8$ sec at -79°C . If conditions were thoroughly simple a linear relationship would be expected, with a slope of $1/\tau_d$. The available range of experimental values cannot, of course, be used to substantiate this expectation. From resistance and capacitance data, the dielectric relaxation time at -79°C can be estimated as approximately 3 seconds. This value is arrived at by measuring the room temperature resistance ($2 \cdot 10^7 \Omega$) at negligible voltage and extrapolating to the low temperature value ($10^{12} \Omega$) on the basis of the known temperature dependence. The capacitance is $3 \cdot 10^{-12}$ F. An accurate value of τ_d cannot be obtained in this way, partly because the capacitance is so small and partly because the extrapolation to -79°C is reliable only as regards order of magnitude. The corresponding slopes are shown on Fig. 4, and are at any rate of the same order if not actually equal. For time intervals less than $10 \mu\text{sec}$, the above re-

sistance value may not be valid because of residual heating (see below). The effects of the screening field are difficult to observe at room temperature since the dielectric relaxation time is then only about 60 μsec .

Thermal Considerations

The temperature of the active region in the film during the ON-state is not precisely known, but it has been established that the current for a given voltage is virtually independent of the ambient temperature. This fact has been variously interpreted as meaning (a) that the ON-state filament is very hot, or (b) that it is very cool. What is certain is that heat losses from the filament are more important at low than at high ambient temperatures. Moreover, some electrode heating must be envisaged during long, but not during short, switching pulses. The effects of heating during the succeeding OFF-state should, therefore, show themselves most sensitively at room temperature and below, e.g. as a decaying increment in OFF-state conductance. Any such decay which takes place within a microsecond or so cannot be distinguished from the free charge-carrier decay. Any (room temperature) effect within 10-30 μsecs may be associated with the dielectric decay. However, any effect existing for longer times (e.g. minutes) may be safely ascribed to thermal factors.

Two successive pulses are applied to the switch; the first is a switching pulse and the second, at lower voltages, probes the increased conductance due to heat generated by the first pulse. The arrangement of measuring circuits is shown in Fig. 5a. Figure 5b shows that the switch is indeed slightly more conductive after the ON-state. The residual conductance remains for about 1 min and it becomes larger as I_{ON} is increased. Since the voltage during the ON-state is nearly constant (high slope of the ON-characteristic), the power dissipation is proportional to I_{ON} . One would thus expect the residual conductance to be likewise proportional to I_{ON} , which is approximately correct.

Figure 5c shows that if the period of the ON-state is lengthened, the recovery time of the switch is also lengthened, but the initial conductance increment is not greatly increased. This suggests the following interpretation: a larger I_{ON} results in a greater temperature rise in the film; the heating process being almost adiabatic if the period of the ON-state is sufficiently short. If the period of the ON-state is long, heat loss to the electrodes (graphite hemispheres in this case), becomes important. The heating process is more nearly isothermal in this case. The larger total mass then involved accounts for the prolonged thermal decay. Comparative measurements carried out at higher ambient temperatures yield longer cooling times and thereby confirm the interpretation in qualitative terms. If the entire conductance increment of 10^{-4} sec is interpreted as thermal, its value corresponds to a temperature increase of 0.1 to 0.2°C for $I_{ON} = 8.7$ mA.

If the source of heat is mainly in the film itself, the cooling process would follow Newton's law, $T = T_a + (T_{ON} - T_a) \exp(-t/\tau_{ON})$, provided that the temperature difference between the ambient temperature, T_a , and the temperature in the interior of the film at the end of the ON-state, T_{ON} , is small. τ_{ON} is the thermal time constant given by the ratio of the heat capacitance of the film to the thermal conductance of the film. Chen⁽¹⁴⁾ has given the molar heat capacitance as 7 cal/mole/deg., the molar volume as 7 cm³/mole and the heat conductivity as $2 \cdot 10^{-3}$ cal/cm/deg. On this basis, and assuming that most of the heat is lost through the electrodes, the thermal time constant would be about 500 or 100 μ sec, and the temperature rise at 10^{-7} sec of the order of 1°C for $I_{ON} \approx 8.7$ mA. Thus, an unusually large discrepancy appears between the observed value of about 1 min for the recovery time and the estimated value, based on the above assumptions. One could, alternatively, assume that the electrodes are heated substantially during the ON-state, and that this heat capacitance must therefore be involved. This would, in principle, explain a greater increased recovery time.

An alternative view can be presented as follows. It is widely agreed that the potential profile along the axis of an ON-state filament is as shown in the insert of Fig. 4. This implies that carriers enter through barriers, the existence of such barriers is also implied by the transient ON-state characteristics described by Pryor and Henisch⁽¹³⁾, and the most likely entry mechanism is tunneling. The question is, within what distance do these carriers thermalize? In the ordinary way (amorphous material in quasi-equilibrium; traps mostly empty), that distance would be very short, e.g. ≈ 50 Å or so. However, very different conditions are believed to prevail during the ON-state. Because of the substantial carrier excess, all traps are likely to be full. In the interior of the switch, this does not entail departure from neutrality, because the concentrations of hole-traps and electron traps is (on independent grounds) believed to be equal. The thermalizing distance may therefore be much greater. The suggestion, here tentatively made, is that distance is greater than the film thickness. The mean-free path is not likely to be very different in the ON- and OFF-states, but there is independent support⁽¹⁵⁾ for the idea that thermalization is more difficult than is ordinarily supposed. If this assumption were correct, it would mean that the injected electrodes thermalize at (and in) the anode. It would account for the fact that (1) the positive electrode appears hotter than the negative one⁽¹⁶⁾ and (2) the electrodes are more readily damaged by heat than the chalcogenide film itself⁽¹⁷⁾. The model would also imply that the "lattice" temperature in the interior is quite low, as suggested by the data on Fig. 5.

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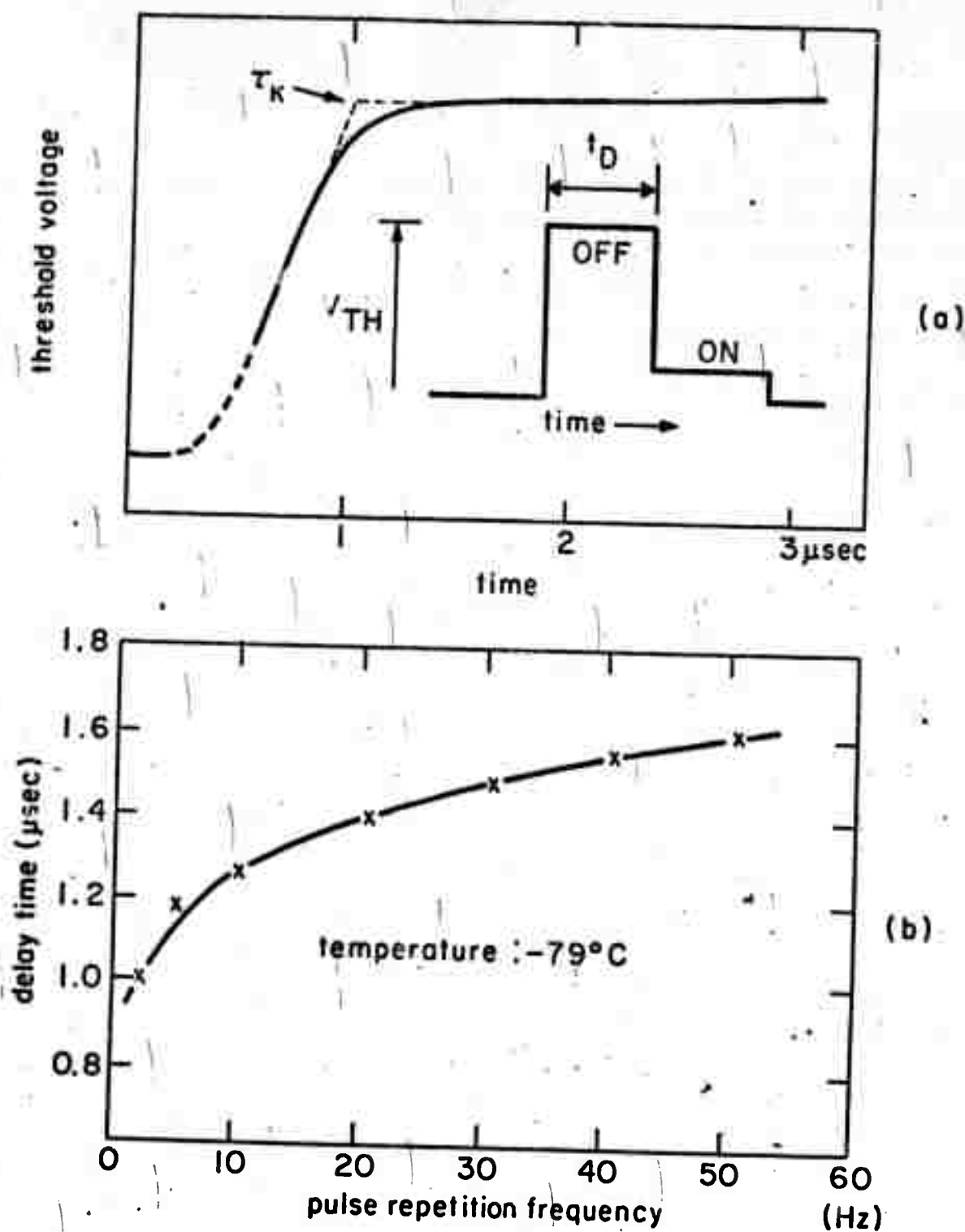


FIG. 1 Response of ovonic switches to successive voltage pulses. (a) schematic relationship between the threshold voltage and the pulse interval (ref. 13). (b) observed relationship between delay time and pulse repetition frequency at constant voltage.

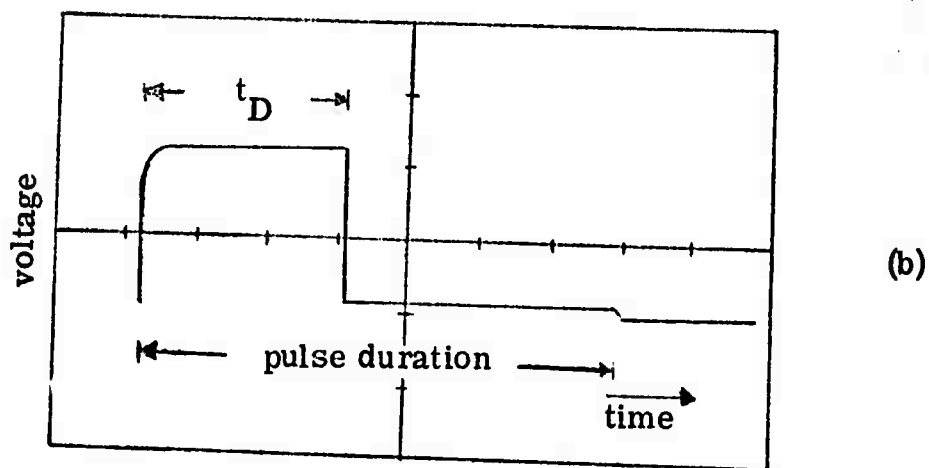
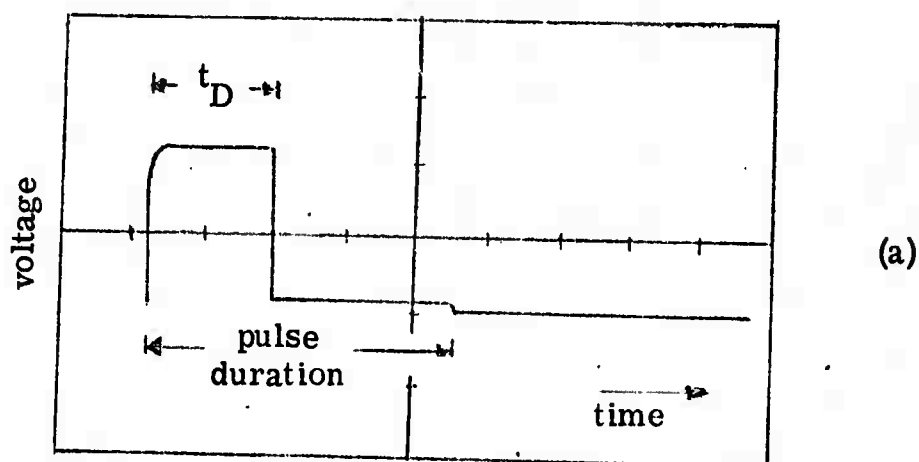
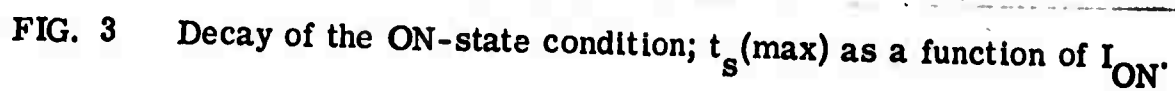


FIG. 2 The relationship between the delay time (t_D) at constant voltage and the total duration of the pulse. Pulse repetition frequency 6Hz. Time scale 1 μ sec/div. Voltage scale: 10V/div. Ambient temp: -79°C . (a) and (b) different pulse durations.



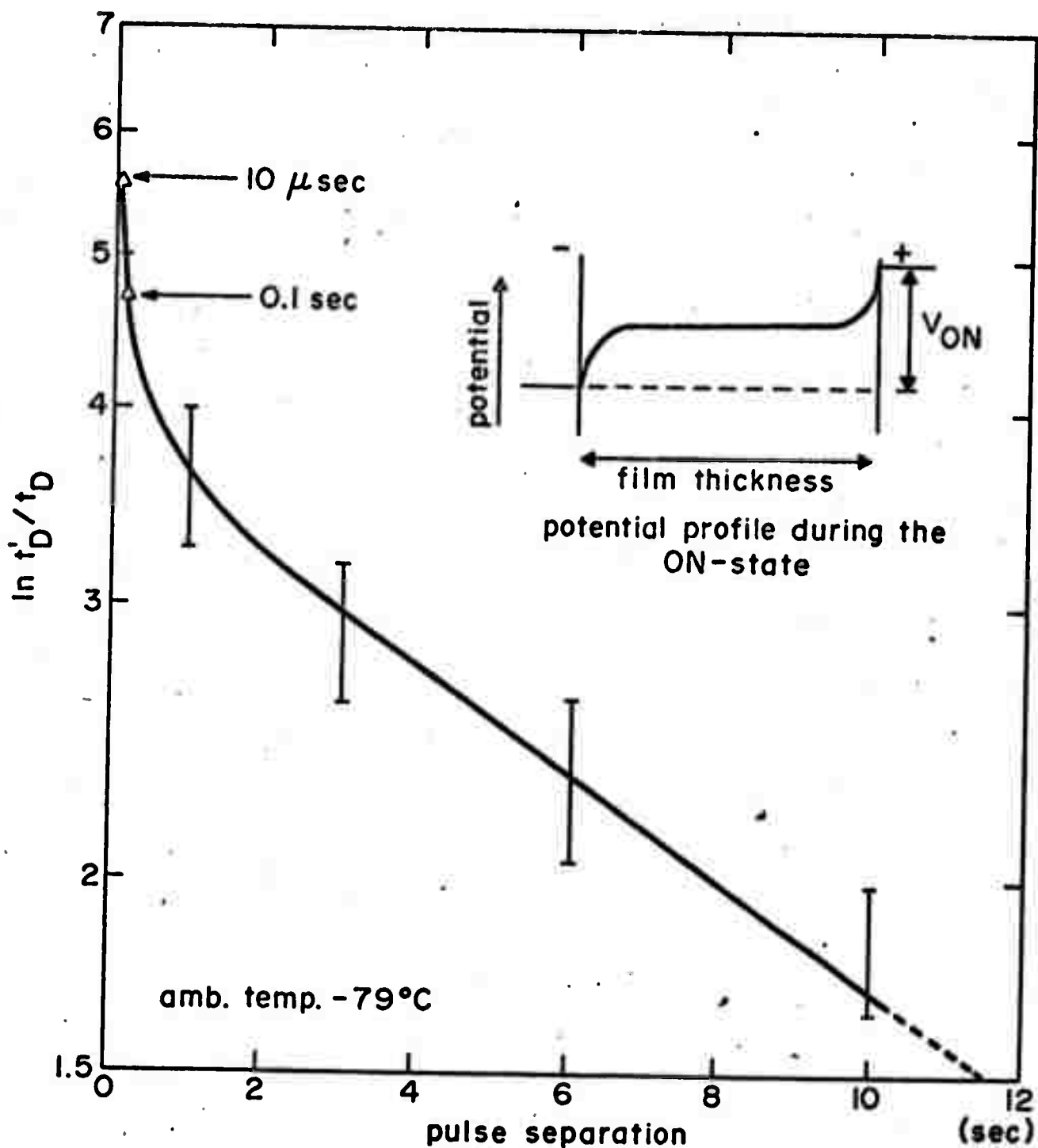


FIG. 4 Recovery of characteristics after a switching event. Pulse pairs at 2 min intervals, separated by times shown:
 t_D = delay time for first pulse
 t'_D = delay time for second pulse, at the same voltage.

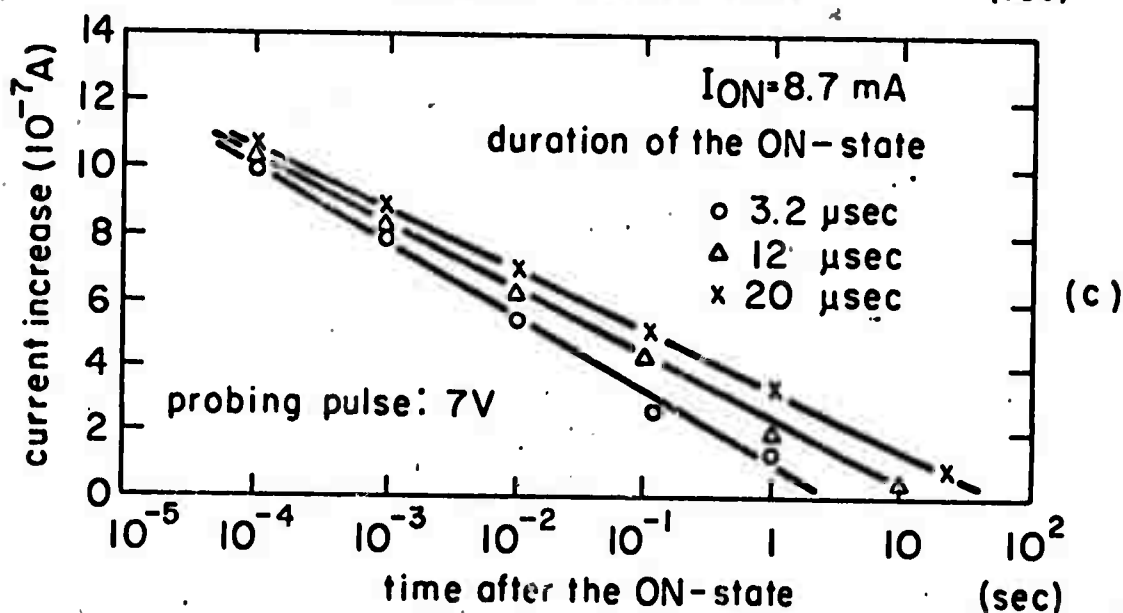
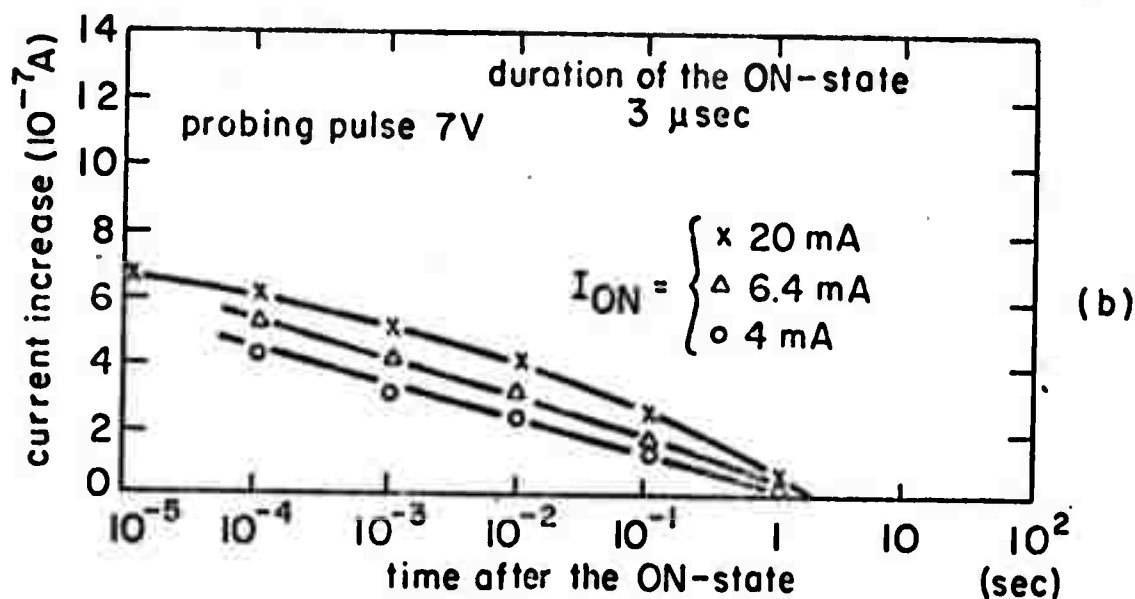
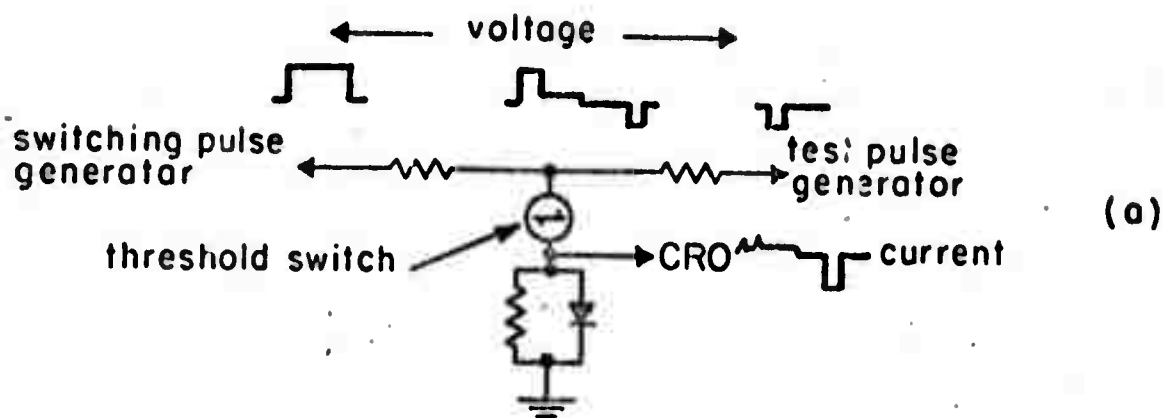


FIG. 5 The decay of the residual conductance after an ON-state.
 (a) measuring circuit. (Diode serves to prevent CRO overload.)
 (b) residual current (at 7 volts) for different values of I_{ON} .
 (c) residual current (at 7 volts) for different ON-periods.